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VOL. XXXIII NOVEMBER, 1956 No. 11

CONTENTS

		PAGE
170.	Synthetic gonadogens. Part II.—By S. M. Mukherji, R. P. Gandhi and V. S. Gaind	765
171.	Common rings. Part I. *cis*-Eliminations.—By Sukh Dev	769
172.	Potentiometric and volumetric estimation of peroxides with alkaline permanganate —By I. M. Issa and H. Khalifa	778
173.	Formation of oxygen complex on charcoal.—By Balwant Rai Puri, Y. P. Myer and Lekh Raj Sharma	781
174.	Hydroxyketones. Part VI. The Fries rearrangement of the phenolic esters of *o*- and *m*-nitrobenzoic acids and some thiophenyl esters.—By G. S. Saharia and B. R. Sharma	788
175.	Chemistry of beryllium. Part I. Formation of beryllates.—By Sarju Prasad and Kashi Prasad Srivastava	791
176.	Condensation products of benzylidene-acetone with substituted thioureas.—By M. K. Rout	796
177.	Steroid sapogenins from Indian Dioscorea plants. Part II.—By A. K. Barua, (Mrs) D. Chakravarti and R. N. Chakravarti	799
178.	Production of 12- and 18-hydroxystearic acids and some useful compounds derived from them.—By A. S. Gupta and J. S. Aggarwal	804
179.	Interaction of thionyl chloride and aromatic hydroxyketones and their derivatives in presence of finely divided copper. Part X. Preparation of 3 : 3′-dibenzoyl-2 : 6-2′ : 6′- and -4 : 6 4′ : 6′-tetrahydroxydiphenyl thioethers and their derivatives.—By V. J. Dalvi and G. V. Jadhav	807
180.	Studies in indigoid dyes. Part XX.—By Paresh Chandra Dutta and Dasrath Mandal	812
181.	The invertase activity of yeast in presence of acids and salts.—By M. M. Biswas ...	815
182.	Interaction of aromatic hydroxyketones and thionyl chloride in presence of finely divided copper. Part XI. Preparation of 2 : 2′-dihydroxy-3 : 3′-diacetyl- and -3 : 3′ dipropionyl-5 : 5′-dimethyldiphenyl sulphides and 2 : 2′-dihydroxy-3 : 3′-dimethyl-5 : 5′-diacetyldiphenyl sulphide.—By V. G. Kulkarni and G. V. Jadhav	818
183.	Studies on the dependence of optical activity on chemical constitution. Part XLIV. The rotatory dispersion of *o*-, *m*-, *p*-chlorophenylimino-*d*-camphors and phenyl-, *o*-, *m*-, *p*-chlorophenylamino-*d*-camphors.—By Bawa Kartar Singh and (Miss) Shanti Kumari Seth	821
184.	Amino derivatives of titanium tetrabromide. Part I.—By Sarju Prasad and Jai Beniprasad Tripathi	838
185.	On the stability of inner-metallic complexes.—By Basudeb Das Sarma and Priyadaranjan Ray	841

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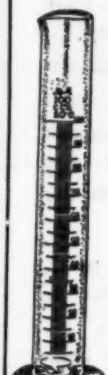

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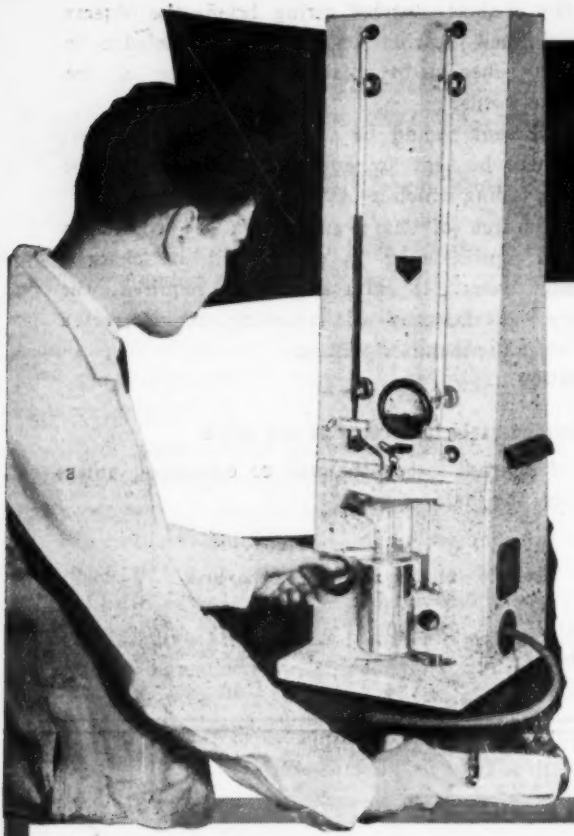

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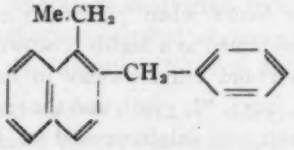
[Jour. Indian Chem. Soc., Vol. 33, No. 11, 1956]

SYNTHETIC GONADOGENS. PART II

By S. M. Mukherji, R. P. Gandhi and V. S. Gaind

The synthesis of 7-(4′-ketocyclohex-2′-enylmethyl)-1 : 9-octalone-2 and 8-ethyl-7-(4′-ketocyclohex-2′-enylmethyl)-1 : 9-octalone-2 as potential androgens has been described herein.

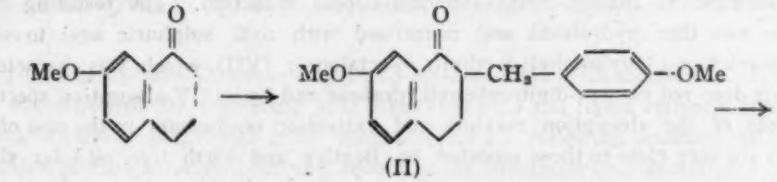
Juday (*J. Amer. Chem. Soc.*, 1953, **75**, 3008, 4017) has placed the derivatives *inter alia* of 1-ethyl-2-benzylnaphthalene (I) among the class of synthetic estrogens. He also observed that 6-hydroxy-1-ethyl-2-(*p*-hydroxybenzyl)-1 : 2 : 3 : 4-tetrahydronaphthalene showed enhanced biological activity as compared to the corresponding *p*-hydroxyphenyl derivative, reported earlier by Dodds *et al.* (*Proc. Roy. Soc.*, 1939, **B127**, 140).



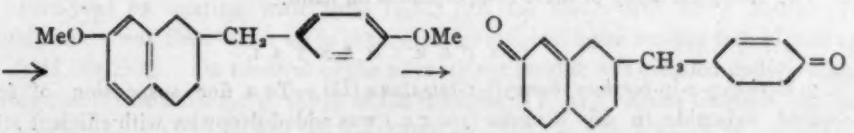
(I)

In view of these findings and also in continuation of the work described in Part I (this *Journal*, 1956, **33**, 709), it was thought of interest to examine for androgenic activity the hydroaromatic structures having 2-benzylnaphthalene moiety. When our work was in progress, Bentley and Firth (*J. Chem. Soc.*, 1955, 2398, 2403) reported the synthesis of the hydroaromatic systems corresponding to 6-hydroxy-2-(*p*-hydroxybenzyl)-1 : 2 : 3 : 4-tetrahydronaphthalene.

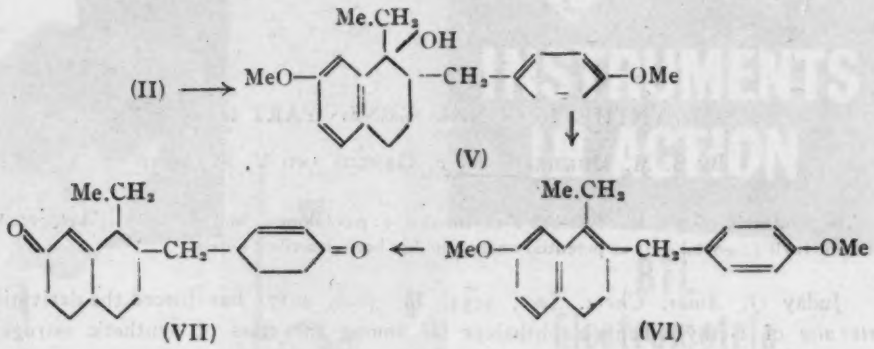
We now report the synthesis of 7-(4′-ketocyclohex-2′-enylmethyl)-1:9-octalone-2 (IV) and 7-(4′-ketocyclohex-2′-enylmethyl)-8-ethyl-1:9-octalone-2 (VII) according to the following scheme :



(II)



(III) (IV)



The starting material, 7-methoxy-2-(*p*-methoxybenzyl)-1-tetralone (II) was prepared in 50% yield by alkylating 7-methoxy-1-tetralone with *p*-methoxybenzyl chloride in presence of sodamide. The tetralone (II) was then reduced by the Clemmensen method (Martin's modification) for fifty hours when 7-methoxy-2-(*p*-methoxybenzyl)-1:2-3:4-tetrahydronaphthalene (III) was obtained as a highly viscous substance in 62% yield, which was reduced with lithium and ethyl alcohol in liquid ammonia (Wilds and Nelson, *J. Amer. Chem. Soc.*, 1953, **75**, 5366), and the resulting tetrahydro derivative was hydrolysed and isomerised with 10% sulphuric acid (cf. Bentley and Firth, *loc. cit.*) to obtain 7-(4′-ketocyclohex-2′-enylmethyl)-1:9-octalone-2 (IV) in 69% yield. This was characterised by its deep red *bis*-2:4-dinitrophenylhydrazone and its U V-absorption spectrum.

Again, 7-methoxy-2-(*p*-methoxybenzyl)-1-tetralone (II) was allowed to react with excess of ethylmagnesium bromide, when it furnished on distillation with a trace of iodine 1-ethyl-7-methoxy-2-(*p*-methoxybenzyl)-3:4-dihydronaphthalene (VI) in 72% yield. The intermediate tertiary carbinol could not be isolated due to spontaneous dehydration during its distillation. The question as to whether the double bond in the endo position as in (VI) or the exo position or both, has not been ascertained as it is of no consequence in the present work so long as the double bond remains conjugated with the benzene ring. However, the compound (VI) could be obtained in a crystalline form, and was subjected to lithium-liquid ammonia-alcohol reduction. The resulting hydro derivative was then hydrolysed and isomerised with 10% sulphuric acid to obtain 7-(4′-ketocyclohex-2′-enylmethyl)-8-ethyl-1:9-octalone-2 (VII), which was characterised through its deep red *bis*-2:4-dinitrophenylhydrazone and by its UV-absorption spectrum. The values of the absorption maxima and extinction coefficients in the case of (IV) and (VII) are very close to those reported by Bentley and Firth (*loc. cit.*) for similar structures.

The biological assay of these compounds is on hand.

* Experimental

7-Methoxy-2-(p-methoxybenzyl)-1-tetralone (II).—To a fine suspension of freshly prepared sodamide in dry benzene (100 c.c.) was added dropwise with efficient stirring

* Melting and boiling points are uncorrected. Analyses by Drs. Weiler and Strauss, Oxford.

a solution of 7-methoxy-1-tetralone (8.8 g.) in dry benzene (50 c.c.). The reaction mixture was allowed to stand overnight and then refluxed on the steam-bath for 15 hours, when the sodium salt of the tetralone separated. To this was then added a solution of *p*-methoxybenzyl chloride (7.8 g.) in dry ether (25 c.c.). After standing for half an hour the mixture was refluxed on the steam-bath for 8 hours. The cooled reaction mixture was then poured on iced HCl. The organic layer was separated and the aqueous layer extracted with benzene. The combined extract was washed free of acid, dried (Na_2SO_4) and stripped off the solvents. The residual mass on distillation under reduced pressure yielded 7.4 g. (50%) of the benzylated product (II) as a stiff substance, b.p. 247-50°/6 mm. On keeping it solidified. Crystallisation from methanol afforded beautiful shining flakes, m.p. 89°. (Found: C, 76.6; H, 6.82. $C_{19}H_{20}O_2$ requires C, 77.00; H, 6.80 per cent).

The 2:4-*dinitrophenylhydrazone* of (II) was prepared by the usual procedure (H_2SO_4 method) except that the reaction mixture had to be heated on the water-bath for half-an-hour when the hydrazone derivative formed slowly as dark red crystals; it was crystallised from ethyl acetate-alcohol mixture as deep red needles, m.p. 200-201°. (Found: N, 11.40. $C_{25}H_{24}O_6N_4$ requires N, 11.76 per cent).

7-Methoxy-2-(p-methoxybenzyl)-1:2:3:4-tetrahydronaphthalene (III).—The above ketone (5.56 g.) was reduced by the Clemmensen method (Martin's modification) with amalgamated zinc wool (10 g.), HCl (conc., 13 c.c.), water (6 c.c.) and toluene (25 c.c.). A negative response in coloration with a drop of 2:4-dinitrophenylhydrazine chloride solution was obtained after 48 hours of refluxing during which period HCl (conc., 3 c.c.) was added every six hours. The organic layer was then taken up completely in ether, the ether-toluene layer washed with water and then stripped off the solvents. The residue, which gave a coloration with alcoholic ferric chloride, thus indicating demethylation, was methylated by refluxing with dimethyl sulphate (5 g.) in acetone (50 c.c.) and potassium carbonate (2.7 g.). After 3 hours, acetone was removed and the carbonate dissolved by addition of iced water. The organic product was taken up in ether and after the usual working up, the residue yielded 3.5 g. (62%) of 7-methoxy-2-(*p*-methoxybenzyl)-1:2:3:4-tetrahydronaphthalene (III) as a viscous mass, b. p. 225°-230°/4 mm. (Found: C, 80.70; H, 7.68. $C_{19}H_{22}O_2$ requires C, 80.81; H, 7.85 per cent).

7-(4'-Ketocyclohex-2'-enylmethyl)-1:9-octalone-2 (IV).—Reduction of (III: 2.82 g.) was accomplished by dissolving it in ether (100 c.c.) and liquid ammonia (150 c.c.) and adding lithium (1.26 g.) and ethyl alcohol (11.1 g.) following exactly the procedure described in Part I (*loc.cit.*) for the reduction of 7-methoxy-2-(*p*-anisyl)-1:2:3:4-tetrahydronaphthalene. The reaction mixture was similarly worked up and the product was hydrolysed by heating with 10% H_2SO_4 on the steam-bath for 5 hours. The organic layer was then taken up in ether and the ethereal layer washed free of acid and then dried (Na_2SO_4). On removal of the solvent, the residue was distilled under reduced pressure and it furnished 1.1 g. (55%) of the diketone (IV) as a viscous colorless oil, b.p. 220°-225°/5 mm., $\lambda_{max.}^{alc.}$ 220 mμ (ε 9,972). (Found: C, 79.10; H, 8.60. $C_{17}H_{22}O_2$ requires C, 79.03; H, 8.58 per cent).

The bis-2 : 4-*dinitrophenylhydrazone* was prepared in the usual way and crystallised from ethyl acetate-alcohol mixture as deep red needles, m p. 120-21° (sintering at 102°). (Found : N, 18.44. $C_{29}H_{30}O_8N_8$ requires N, 18.12 per cent).

7-*Methoxy*-1-*ethyl*-2-(p-*methoxybenzyl*)-3 : 4-*dihydronaphthalene* (VI).—To a cooled solution of ethylmagnesium bromide (from 4.4 g. ethyl bromide, 0.96 g. Mg and 20 c.c. anhydrous ether) was added dropwise a solution of 7-methoxy-2-(*p*-methoxybenzyl)-1-tetralone (II, 5.9 g.) in dry thiophene-free benzene (30 c.c.). After 2 hours the mixture was refluxed on the steam-bath for 6 hours and then decomposed with iced HCl. The hydrolysate was extracted with ether and the ethereal extract was freed of acid and dried (Na_2SO_4). The solvent was aspirated and the residual oil distilled under reduced pressure in presence of a trace of iodine, when 4.4 g. (72%) of 7-methoxy-1-ethyl-2-(*p*-methoxybenzyl)-3 : 4-dihydronaphthalene (VI) was obtained, b.p. 230°-235°/5 mm., which solidified on keeping, and on crystallisation twice from methyl alcohol it melted at 102°. (Found : C, 80.86 ; H, 7.84. $C_{20}H_{24}O_2$ requires C, 81.04 ; H, 8.16 per cent).

7-(4′-*Ketocyclohex*-2′-*enylmethyl*)-8-*ethyl*-1 : 9-*octalone*-2 (VII).—A solution of (VI, 3.08 g.) in anhydrous ether (100 c.c.) and liquid ammonia (200 c.c.) was reduced with lithium (1.26 g.) and ethyl alcohol (11.1 g.), following exactly the procedure described for the reduction of 1-ethyl-2-(*p*-methoxyphenyl)-7-methoxy-3 : 4-dihydronaphthalene (this *Journal*, 1956, **33**, 714). Hydrolysis and migration of the double bonds to $\alpha\beta$-positions were effected by treatment with 10% H_2SO_4 on the steam-bath for 5 hours. The hydrolysate was taken up in ether, the ethereal layer washed free of acid and dried (Na_2SO_4). After removal of the solvent the residue gave 1.8 g. (62%) of 7-(4′-ketocyclohex-2′-enylmethyl)-8-ethyl-1 : 9-octalone-2 (VII) as a colorless viscous oil, b.p. 225-28°/5 mm., $\lambda_{max.}^{alc.}$, 222 mμ (ϵ 10,021). (Found : C, 80.05 ; H, 8.80. $C_{19}H_{26}O_2$ requires C, 79.70 ; H, 9.09 per cent).

The bis-2 : 4-*dinitrophenylhydrazone* of the above ketone was prepared in the usual way and crystallised from ethyl acetate-alcohol mixture in deep orange plates, m.p. 135° (sintering at 120°). (Found : N, 17.70. $C_{31}H_{34}O_8N_8$ requires N, 17.34 per cent).

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COMMON RINGS. PART I. *cis*-ELIMINATIONS

By Sukh Dev

Based on stereochemical considerations, it has been pointed out that the ease of ionic 1:2-*cis*-eliminations in various suitably constituted derivatives of common rings should follow the order : *cyclo*pentane ≃ *cyclo*heptane > *cyclo*hexane. Qualitative data are presented, which appear to support this hypothesis.

*cyclo*Alkanes and their derivatives form a unique series, wherein the differences in the various chemical and physical properties of a given class of compounds arise essentially as a consequence of the three dimensional geometry of the rings. This concept has been advocated, especially, by Prelog *et al.* (*J. Chem. Soc.*, 1950, 420) and Brown and his co-workers (*J. Amer. Chem. Soc.*, 1951, **73**, 212 ; 1952, **74**, 1894 ; Brown, *Record of Chemical Progress*, 1953, **14**, 83) to explain the differences in the behaviour of the various members differing in ring-size. The treatment, apparently, is not satisfactory in the case of small-ring compounds, where other factors must also be operative (Roberts and Chambers, *J. Amer. Chem. Soc.*, 1951, **73**, 5034).

In the common rings*, Baeyer's classical strain (*Ber.*, 1885, **18**, 2269, 2277) is almost absent and the differences in the energy-content (Spitzer and Huffman, *J. Amer. Chem. Soc.*, 1947, **69**, 211) arise essentially from the non-bonded interactions of the polymethylene chain. While preserving the tetrahedral valency angles, the *cyclo*pentane ring can be built only from the energetically unfavourable, eclipsed constellations (conformations) of the polymethylene chain ; according to Pitzer (*Science*, 1945, **101**, 672) this geometrically preferred model of *cyclo*pentane does not visualise the actual picture of the molecule, which can gain extra stability by assuming a non-planar conformation (Fig. 1), when the strain due to non-bonded interactions (Pitzer strain) will be somewhat relieved.

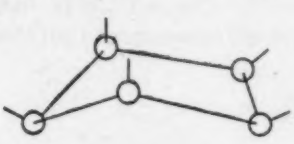


Fig. 1

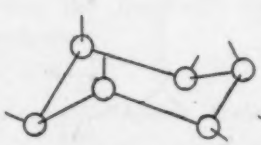


Fig. 2

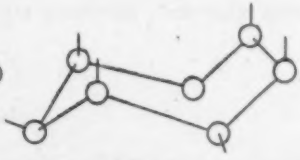


Fig. 3

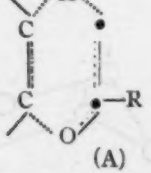
For *cyclo*hexane, the chair conformation (Fig. 2) has been shown to be more stable, both on thermodynamic considerations (Aston *et al.*, *J. Amer. Chem. Soc.*, 1941, **63**, 2029 ; Beckett *et al.*, *ibid.*, 1947, **69**, 2488) and on physical evidence (Rasmussen, *J. Chem. Phys.*, 1943, **11**, 249 ; Hassel and Viervoll, *Acta Chem. Scand.*, 1947,

* The classification of ring-compounds into small rings (3- & 4-membered), common-rings (5-, 6- & 7-membered), medium rings (8- to 12- membered) and large rings (13-membered and larger) as suggested by Profs. Brown and Prelog (*J. Amer. Chem. Soc.*, 1951, **73**, 215 ; foot-note 21) is adopted.

1, 149 ; et seq.). *cyclo*Heptane ring, like *cyclo*hexane, can also exist in two strainless (classical) non-planar constellations ; from models it can be qualitatively deduced that the chair conformation (Fig. 3) will have lesser Pitzer-strain (Sukh Dev, this *Journal*, 1954, **31**, 4) to the extent of about 2.8 k. cals.*

In the transition state of a chemical reaction requiring a synchronous action, the various atoms of importance must occupy a planar configuration for maximum efficiency ; this is undoubtedly due to the efficient overlapping of the concerned orbitals which can result from such a configuration. Barton and co-workers have pointed out the importance of such a concept for various 1 : 2-*trans*-eliminations (Barton and Miller, *J. Amer. Chem. Soc.*, 1950, **72**, 1066 ; Barton and Rosenfelder, *J. Chem. Soc.*, 1951, 1048 ; Barton, *ibid.*, 1953, 1027) and this theory has been utilised by several workers to rationalise various E2-type eliminations (Cristol and Hause, *J. Amer. Chem. Soc.*, 1952, **74**, 2193 ; Evans and Shoppe, *J. Chem. Soc.*, 1953, 540), S$_N$2-type Wagner substitutions (Hiskey, Hirschmann and Wendler, *J. Amer. Chem. Soc.*, 1953, **75**, 5135 ; Hirschmann *et al.*, *ibid.*, 1954, **76**, 4013 ; Elks *et al.*, *J. Chem. Soc.*, 1954, 1739 ; Ames *et al.*, *ibid.*, 1954, 1905), E2-Wagner-eliminations (e.g., see cases cited by Hirschmann *et al.*, *loc. cit.*), Tiffeneau rearrangement (McCasland, *J. Amer. Chem. Soc.*, 1951, **73**, 2293 ; Pollak and Curtin, *ibid.*, 1950, **72**, 961 ; Ramirez and Stafief, *ibid.*, 1955, **77**, 134) and deaminations (Mills, *J. Chem. Soc.*, 1953, 260 ; Cremlyn *et al.*, *ibid.*, 1953, 1847). The much enhanced solvolysis rate of *iso*bornyl chloride, as compared to that of bornyl chloride, has also been explained by Winstein *et al.* (*J. Amer. Chem. Soc.*, 1952, **74**, 1127) as being due to the co-planarity of the atoms involved in the case of *iso*bornyl halide (cf. Ingold, *J. Chem. Soc.*, 1953, 2845).

This importance of co-planarity of the centres concerned has also been stressed in the case of E1-eliminations (Barton, *ibid.*, 1949, 2174; Barton and Rosenfelder, *loc. cit.*). Thus, in reactions involving 1 : 2-*cis*-eliminations, the transition state (A) must have a planar configuration.



(A)

By considering the above models of common rings, it can be seen that, whereas in the case of *cyclo*pentane and *cyclo*heptane, the four atoms (2 carbons and 2 *cis*-substituents) of importance for a *cis*-elimination can acquire a co-planar configuration without altering the preferred constellations of the rings, the corresponding *cyclo*hexane analogue cannot do so. Thus, in the case of a *cyclo*hexane derivative, the configuration of the transition state will differ appreciably from that of the ground state, whereas no such difference will exist in the case of the corresponding five- and seven-

* Prof. R. B. Turner has kindly informed the author that this value is quite reasonable.

membered analogues. This will be reflected in a higher activation energy* for the *cyclo*hexane derivative, and consequently in this system 1 : 2-*cis*-eliminations should be *slower* as compared to those in the analogous *cyclo*pentane and *cyclo*heptane compounds. Of course, this does not apply to those *cyclo*hexane derivatives, in which the ring has been forced to acquire the boat conformation [e.g., when locked by the presence of a 1:4-bridge or by incorporation in a suitable tricyclic system ; cf., Shoppee, *Chem & Ind.*, 1952, 86).

Conversely, 1 : 2-*trans*-eliminations should be faster in a *cyclo*hexyl derivative (with axial disposition of the substituents) as compared to those in an analogous compound with five-membered ring.

Another factor, which will influence the rate of an elimination reaction, is the ease with which the common rings will accommodate an ethylenic linkage. From the heats of hydrogenation of simple cyclic mono-olefines (for data vide Ketelaar, "Chemical Constitution", Elsevier Publishing Co., Amsterdam, 1953, p. 205) it may be concluded that the ease of incorporation of the olefinic linkage will decrease in the order :

*cyclo*Heptane $\rangle$ *cyclo*Pentane $\rangle$ *cyclo*Hexane.

Thus, this second factor should facilitate 1 : 2-elimination in the *cyclo*heptane and *cyclo*pentane rings relative to the *cyclo*hexane system. In a *cis*-elimination, both these factors will operate in the same direction so as to enhance the elimination rate in the seven- and five-membered rings.

In order to test this hypothesis, some comparative *cis*-eliminations have been carried out (*vide infra*) and the results appear to support the predicted behaviour of the common rings. A superior data on this could have been obtained by a kinetic study of a unimolecular *cis*-elimination reaction taking place at temperatures not exceeding 100°. It is realised that at higher temperatures (required for the pyrolysis of esters) the expected energy-hill difference will tend to become less prominent, more so, because at elevated temperatures the boat conformation of *cyclo*hexane assumes importance (Beckett *et al.*, *loc. cit.*). However, the qualitative data presented definitely point towards the correctness of the hypothesis.

Pyrolysis of Cyanohydrin Acetates

It is now well established that the pyrolysis of acetates to yield olefines and acetic acid is a unimolecular reaction, which proceeds by a *cis*-elimination mechanism (Hurd and Blunk, *J. Amer. Chem. Soc.*, 1938, **60**, 2419; Barton, *loc. cit.*; Alexander and Mundrak,

* This extra activation energy may be estimated roughly by determining the difference in the energy content between the chair conformation of *cyclo*hexane and the next stable conformation of *cyclo*hexane having at least one "eclipsed" interaction of the *n*-butane type. A study of the models reveals that such an arrangement can only be the boat conformation of *cyclo*hexane. Thus, the difference in the energy-content of the chair and boat constellations [5.6 k. cal. Turner, *J. Amer. Chem. Soc.*, 1952, **74**, 2118] can be a measure of the extra activation energy.

J. Amer. Chem. Soc. 1950, **72**, 1810, 3194 ; 1951, **73**, 59]. The decomposition of the cyanohydrin acetates of *cyclo*pentanone, *cyclo*hexanone and suberone has been investigated under exactly identical conditions and the results* obtained (Table I) are in agreement with the theory outlined above.

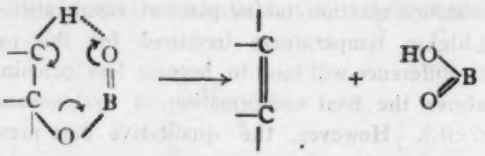
TABLE I

No.	Temp.	Δ^1-*cyclo*Pentenyl nitrile.	Δ^1-*cyclo*Hexenyl nitrile. (% yield per pass)	Δ^1-*cyclo*Heptenyl nitrile.
1.	440° ± 2°	65.8	59.0	82.6
		67.0	59.1	82.0
2.	460° ± 2°	92.0	80.0	93.6
		90.0	79.0	91.4

The above results also reveal the superiority of the cyanohydrin acetate decomposition method for the preparation of unsaturated nitriles of the common rings ; the overall yields based on the starting ketone are over 80% (vide Experimental).

Decomposition of Borates

Brandenberg and Galat (*J. Amer. Chem. Soc.*, 1950, **72**, 3275) reported the use of boric acid for the dehydration of alcohols ; O'Connor and Nace (*ibid.*, 1953, **75**, 2118) later suggested that this reaction proceeded *via* the unstable metaborate esters, which underwent *cis*-elimination to yield the olefine :



This reaction ** has been applied to the dehydration of the *cyclo*alkanols of the common rings and the results obtained have been recorded in Table II, and the order of decomposition temperatures is the expected one.

* In the advance communication on the pyrolysis of *cyclo*pentanone cyanohydrin acetate (Dev, *Experi.*, 1954, **10**, 60) comparison with the pyrolysis of *cyclo*hexane cyanohydrin acetate was based on the published data (Burus *et al.*, *J. Chem. Soc.*, 1935, 400) ; the slightly different results described are more stable, as the comparative decomposition of the acetates has been carried out under exactly identical condition.

** The preparation of the meta-borates is more conveniently carried out by azeotropic distillation (vide Experimental) with toluene The pyrolysis of the borates should prove to be the method of choice for the dehydration of alcohols, especially secondary and primary. It is hoped to determine the scope of this reaction in a future communication.

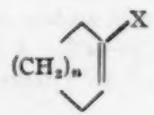
TABLE II

	Metaborate of		
	*cyclo*Pentanol.	*cyclo*Hexanol.	*cyclo*Heptanol.
Decomp. temp. (initial)	220°	235-240°	220-225°
Decomp. temp. ("progress")	185°-190°	215°	200°

Light Absorption Data

The ultraviolet spectra of the Δ^1-nitriles and the acids and esters derived from them are presented in Table III.

TABLE III

Light absorption for 

	X = CN.		X = COOEt.		X = COOH.	
n.	λ max.	ε.	λ max.	ε.	λ max.	ε.
1.	214 mμ	10,090	223 mμ	8,654	† 221 mμ	10, 280
2.	<211 *	11,290	219	11,260	† 216 218	0 210 10, 270
3.	214	10,310	221	9,854	† 220	9, 057

* Cf. Braude and Wheeler, *J. Chem. Soc.*, 1955, 327.

† Cf. Braude and co-workers, *ibid.*, 1951, 1755; 1950, 2014; 1953, 2204; Ungnade and Ortega, *J. Amer. Chem. Soc.*, 1951, **73**, 1564.

These data indicate that the *cyclo*pentane and *cyclo*heptane derivatives of this type show a bathochromic shift of approximately 4 ± 2 mμ as compared to the corresponding *cyclo*hexane compounds. A search of the literature reveales that this conclusion applies to various other cases with (X = CHO, $COCH_3$, COC_6H_5, C≡CH, etc.). A complete discussion of this will form the subject matter of a further communication.

EXPERIMENTAL

Melting and boiling points are uncorrected. The ultraviolet absorption spectra were determined in 95% ethanol solution on a Beckman spectrophotometer (Model DU). Petroleum ether refers to the fraction of b.p. 40°-60°.

cyclo*Pentanone Cyanohydrin Acetate*.—To thoroughly chilled (ice-salt) *cyclo*pentanone (126 g., 1.5 *M*) liquid HCN (48.6 g., 75 c.c., 1.8 *M*) was added in one lot. To this powdered potassium cyanide (0.2 g.) and diethylamine (0.2 c. c.) were introduced, and after keeping the mixture at -10° for ½ hour, it was allowed to stand in the Frigidaire for 24 hours. The product was chilled to -5° and the base neutralised by the addition of phosphoric acid (85%, 1 c.c.). After dilution with anhydrous ether (75 c.c.), the material was again well chilled and a mixture (also cooled to about -5°)

of acetic anhydride (240 c.c.) and acetyl chloride (10 c.c.) added. This was left aside at 0° for 48 hours and then at room temperature (25°-30°) for another 4½ days. The excess acetic anhydride, etc. were removed through a column (Vigreux ; 8″) and the residue carefully fractionated to obtain the required compound as a colorless, mobile liquid, b. p. 120°/15 mm., 137°/30 mm., n_D^{30} 1.4455 ; yield 216-223 g. (94-97%). The acetate can be distilled without any decomposition ; b.p. 226-27°/684 mm. A purified sample (refractionation, central cut) had n_D^{30}, 1.4460 ; d_4^{30}, 1.053 ; M_D, 38.77 (calc. 38.35). (Found : C, 62.6 ; H, 7.5. $C_8H_{11}O_2N$ requires C, 62.7 ; H, 7.2 per cent).

When the reaction mixture was worked up before acetylation, the cyanohydrin could be isolated in 92-94% yield ; b.p. 130°/26 mm., n_D^{31}, 1.4555. A purified sample had n_D^{31}, 1.4540 ; d_4^{31}, 1.022 ; M_D, 29.41 (calc. 28.99) (Cook and Linstead, *J. Chem. Soc.*, 1934, 959, report b.p. 126°/26 mm.).

cyclo*Hexanone cyanohydrin acetate* was prepared exactly as above ; b.p. 148-49°/35 mm., m.p. 48-49°, yield 91-94%. A sample was recrystallised from *n*-hexane in large colorless prisms, m.p. 48-50° [Burns, Jones and Ritchie, *loc. cit.*, report 45.8% yield, m.p. 48-49°].

cyclo*Heptanone Cyanohydrin Acetate*.—By following the procedure outlined above for the *cyclo*pentanone derivative, the seven-membered analogue was obtained as a colorless liquid, b.p. 163°/37 mm., 146°/15 mm., n_D^{28} 1.4650, yield 91-95%. [Found : N, 7.9. $C_{10}H_{15}O_2N$ requires N, 7.7 per cent].

Pyrolysis of Cyanohydrin Acetates.—One end of a thick Pyrex-tube (50 cm ; I.D. 1.9 cm.) was bent at an angle of 120°, and to the other end another tubing (45 cm ; I.D. 0.9 cm.) carrying a B-19 cone was fused ; the cone fitted into a Y-shaped adapter, which, in turn, was connected to a water-condenser and a receiver. The wider-tube was filled with broken Pyrex-glass chips (average length 1 cm.) to a length of 20 cm. (measured from the constriction). The packed portion of the tube was heated in an electric furnace ; the required temperature (as determined by a thermocouple) was maintained by a Sunvic control. The furnace, carrying the pyrolysis tube, was held at a slight angle (about 20°).

The pyrolysis at the required temperature was carried out by dropping in the cyanohydrin acetate (0.15 *M*) during 11 minutes ; the addition was made in three or four lots so that the temperature and the time could be effectively controlled. The receiver was cooled in an ice-bath. After the pyrolysis, the furnace was allowed to cool to about 100° and *n*-hexane (15 c.c.) was let in as a "chaser" to remove the last traces of the material. The product (pyrolysate + "chasings") was taken up in petroleum ether (50 c.c.), washed with water (50 c.c.) and finally with brine (50 c.c. × 2) and dried (Na_2SO_4). The solvent was removed (column) and the residue carefully fractionated through a Vigreux column with a total-condensation-type still head. The results are recorded in Table I.

Δ^1-cyclo*Pentenyl Nitrile*.—For preparative purposes, the pyrolysis was best carried out at around 470° ; 2 g. of the acetate was let in during one minute. In this way the unsaturated nitrile was obtained in 95-98% yield. The product, which had a strong odour of bitter almonds had b.p. 88-89°/54 mm., n_D^{31} 1.4670-1.4690. A purified sample (refractionation ; central cut) gave b.p. 75°/35 mm., n_D^{27} 1.4700 (Cook and Linstead,

loc. cit., obtained this nitrile by the dehydration of the cyanohydrin with thionyl chloride in benzene and the yield was 55-60% and b.p. 69°/15 mm. Also vide Baker and Leeds, *ibid.*, 1948, 977).

Δ^1-cyclo*Hexenyl nitrile* was prepared in 93-97% yield by conducting the pyrolysis of the cyanohydrin acetate at about 480° and by passing the acetate at the rate of 2 g./min. (cf. Burns, Jones and Ritchie, *loc. cit.*). The material had b.p. 118°/65 mm., n_D^{22}, 1.4780–1.4770 and possessed an intense odour of bitter almonds. A purified sample had b.p. 99°/35 mm., n_D^{17} 1.4780 [Kidd, Robins and Walker, *J. Chem. Soc.*, 1953, 3244, prepared the nitrile in 94% yield by the dehydration of the cyanohydrin with phosphoryl chloride in pyridine ; b.p. 85-90°/17 mm., n_D^{19} 1.4864. Cf. Ruzicka and Brugger, *Helv. Chim. Acta*, 1926, **9**, 399 ; Bhattacharyya, this *Journal*, 1945, **22**, 87].

Δ^1-cyclo*Heptenyl Nitrile*.—By following the conditions stated above for the five-membered analogue, the *cyclo*heptenyl nitrile was obtained in 96-99% yield. This had only a mild odour of bitter almonds and had b.p. 116-18°/35 mm., n_D^{17}, 1.4845–1.4850. A refractionated sample gave b.p. 118°/35 mm., n_D^{17}, 1.4850. (Found : N, 11.24. $C_9H_{11}N$ requires N, 11.54 per cent).

Ethyl cyclo*alkenyl carboxylates* were obtained from the corresponding nitriles (0.12 *M*) by heating them with absolute ethyl alcohol (80 c.c.) and H_2SO_4 (C.P., 20 c.c.) on a steam-bath for 24 hours (silica-gel guard tube). The coloured (orange to brown) reaction mixture, which deposited a lot of ammonium sulphate on cooling, was diluted with water (250 c.c.) with ice-cooling. The ester layer was separated and the aqueous phase extracted with petroleum ether (30 c.c. × 3). The combined extracts were mixed with the main lot and washed with brine (25 c.c. × 3) and dried (Na_2SO_4). The material was stripped off the solvent and the residue fractionated through a helices-packed column (6″) with a total-condensation-type still head. The esters were colorless oils with pleasant odour ; yield 70-75%.

The *ethyl* Δ^1cyclo*pentenyl carboxylate* had b.p. 95°/35 mm., n_D^{17}, 14600 (Cook and Linstead, *loc. cit.*, reported b.p. 92°/25 mm.).

Ethyl Δ^1-cyclo*hexenyl carboxylate* gave b.p. 109°/35 mm., n_D^{17}, 1.4695 (Gardner and Rydon, *J. Chem. Soc.*, 1938, 48, recorded b.p. 95-97°/15 mm., n_D^{16}, 1.4716).

Ethyl Δ^1-cyclo*heptenyl carboxylate* had b.p. 125°/35 mm., n_D^{22}, 1.4770. (Found : C, 71.5 ; H, 9.4. $C_{10}H_{16}O_2$ requires C, 71.4 ; H, 9.5 per cent). As is apparent from the light absorption data (Table III), as well as the acid hydrolysis to the parent acids (*vide infra*), the ethyl esters prepared by the above procedure are essentially pure Δ^1-isomers.

cyclo*Alk* 1-*ene-carboxylic acids* were prepared by two methods : (*i*) Acid hydrolysis of the ester and (*ii*) alkaline hydrolysis of the nitrile.

Method (*i*).—The unsaturated ester (0.1*M*), HCl (C. P., 50 c.c.), acetic acid (25 c.c.) and water (25 c.c.) were mixed and gently refluxed for five hours. In the case of cyclo*pent*-1-*ene-carboxylic acid*, the reaction mixture was chilled to 0° for several hours and the acid, m.p. 120-22°, collected by filtration, yield 85-90%. A sample was recrystallised from *n*-heptane in white prisms, m.p. 122-23° (Haworth and Perkin, *J. Chem. Soc.*, 1894,

65, 101, report m.p. 119-21°). The other two acids were isolated by diluting the reaction mixture with water (100 c.c.), followed by extraction with ether (50 c.c. × 3). The combined extracts were washed with dilute ammonium hydroxide solution (10%; 50 c.c. × 3) and the ammoniacal extract acidified with hydrochloric acid, saturated with sodium chloride, and the acid taken up in petroleum ether (50 c.c. × 3). The petroleum ether solution was washed with brine and dried (Na_2SO_4). The solvent was flashed off (column) and the residue fractionated. The cyclo*hex-1-ene-carboxylic acid* was obtained as an oil, which crystallised on chilling, b.p. 130°/6 mm., n_D^{25} 1.4990; m.p. 33-35°, yield 80%. A sample was recrystallised from petroleum ether at -10° as colorless prisms, m.p. 37-38° (Von Auwers and Krullpfeiffer, *Ber.*, 1915, **48**, 1396, report m.p. 38-39°; Braude and Coles, *loc. cit.*, m.p. 37°; Kidd, Robins and Walker, *J. Chem. Soc.*, 1953, 3244: b.p. 138-41°/18 mm., n_D^{21}, 1.5010). The cyclo*hept-1-ene-carboxylic acid* was isolated in 75% yield, b.p. 117°/1 mm., m.p. 47-48.5°. A sample was recrystallised from *n*-hexane as white plates, m.p. 49-50° (Willstätter, *Annalen*, 1901, **317**, 239, reported m.p. 50-51°; Braude, Forbes and Evans, *loc. cit.*, recorded m.p. 49°).

Method (ii).—The unsaturated nitrile (0.12*M*) was gently refluxed with KOH (13.4 g., 0.24 *M*) in water (130 c.c.) for 40 hours. The cooled solution was acidified to p_H 2.0 with HCl (conc.) and the separated acid isolated as above. cyclo*Pent-1-ene-carboxylic acid* was obtained in 62% yield, m.p. 120-22°, and cyclo*hex-1-ene-carboxylic acid* in a yield of 80%; n_D^{25} 1.4975, m.p. 27-28°; the cyclo*hept-1-ene-carboxylic acid* was prepared in a yield of 77-80% and had m.p. 42-46°. These constants indicated that some isomerisation of the Δ^1- to the Δ^2-isomer had taken place under the alkaline conditions in the *cyclo*hexene and *cyclo*heptene acids.

Pyrolysis of Borates.—A mixture of the alcohol (0.5 *M*), boric acid (0.5 *M*) and toluene (50 c.c.) was placed in a flask (300 c.c.), which carried a thermometer, well reaching to almost the bottom of the flask; a modified Dean-Stark apparatus (Sukh Dev, this *Journal*, 1953, **30**, 443) was attached, and the mixture gently refluxed with continuous removal of water. The separation of water (about 19 c.c.) generally ceased after about 3 hours, when the toluene was distilled off, first as such, later under vacuum (water-pump); the temperature of the bath was not allowed to rise beyond 120°-140°. The residue, which represented the metaborate, crystallised out on cooling.

To the flask containing the borate, a fractionating column (Vigreux, 35 cm., vacuum insulated and carrying a total-condensation-type still head) was attached and the borate slowly heated. In the case of *cyclo*pentanol and *cyclo*heptanol, the esters melted at about 80° and 100° (inside temperature) respectively, whereas the *cyclo*hexyl borate melted at 215°-225°. On further heating, the decomposition started with the generation of the olefine; these temperatures ("initial") have been recorded in Table II; immediately below (about 5°) these temperatures, the esters appeared to boil without decomposition. As the pyrolysis proceeded, the inside temperature fell and the distillation of the olefine was quite smooth at a much lower temperature "(Temperature of decomposition "progress"—Table II). The distillate was worked up for isolation of the olefine.

cyclo*Pentene*.—The distillate, which was collected in a receiver cooled in an ice-salt-bath, contained traces of water and was dried over activated silica gel (−100 mess;

3 g.) at 0° for several hours, and then fractionated over sodium (some dry xylene was used to wash out the silica gel ; the xylene also served as a "chaser"). The olefine was collected at 41°/684 mm.. n_D^{25} 1.4208 ; yield 88-90% (McCasland and Smith, *J. Amer. Chem. Soc.*, 1950, **72**, 2193, report b p. 43-46° ; n_D^{25} 1.4218. Cf. Kogl and Ultee, *Rec. trav. chim.*, 1950, **69**,, 1582).

cyclo*Hexene*, b.p. 78-80°/684 mm., was similarly isolated in a yield of 90%.

cyclo*Heptene*.—In this case petrol fraction (30°-40°) was used in place of xylene for removing the last traces of the olefine from the silica gel. The material had b.p. 110-11°/684 mm., n_D^{25} 1.4575, yield 85% (Kohler *et al.*, *J. Amer. Chem. Soc.*, 1939, **61**, 1059, report b.p. 114.38°/760 mm ; n_D^{20} 1.4580. Cf. Jackson, *ibid.*, 1933, **55**, 4284 ; Boeseken and Hanegraef, *Rec. trav. chim.*, 1942, **61**, 69).

cyclo*Heptanol* required for these investigations was prepared from suberone by the following methods of reduction.

(*i*) *By Meerwein-Ponndorf Reduction*.—The reduction was carried out by closely following the procedure described for the preparation of 5-oxybenzosuberan [Sukh Dev, this *Journal*, 1953, **30**, 799]. The acetone-test became negative after about 42 hours. The product was isolated by extraction with petroleum ether, washing with brine, drying (Na_2SO_4) and fractionation ; b.p. 180°/684 mm., n_D^{20} 1.4725, yield 88-90%.

(*ii*) *By Lithium Aluminium Hydride Reduction*.—Suberone (22.4 g., 0.2 *M*) was reduced with $LiAlH_4$ (2.85 g., 0.075 *M*) in anhydrous ether (150 c.c.) in the usual manner ; yield 97-99%.

(*iii*) *Sodium-iso*Propanol *Reduction*.—In an one-litre 3-necked flask, sodium (13.8 g., 0.6 g. atom) was covered with toluene (80 c.c.). This was heated in an oil-bath (120°-130°) till the sodium melted ; the flame was removed and with vigorous stirring a mixture of the ketone (22.4 g., 0.2 *M*) and *iso*propyl alcohol (36 g., 0.6 *M*) was introduced during 15 minutes (so that the refluxing was controllable) ; toluene (20 c.c.) was used to wash in the last traces of the ketone-alcohol mixture. The colorless reaction mixture was stirred and refluxed (under nitrogen atmosphere) till all the sodium disappeared (about one hour). The product was cooled in ice and cautiously treated with ice-water (about 500 c.c.). The toluene layer was separated, the aqueous phase extracted with petroleum ether (50 c.c. × 2) and added on to the main lot, which was washed with brine (50 c.c. × 3) and dried. The solvent was removed (column) and the residue fractionated ; b.p. 180°/684 mm., n_D^{20} 1.4740, yield 85-90%.

Light Absorption Measurement.—In view of the work of Ungnade and Ortega (*loc. cit.*) the spectra were taken on approximately 0.5 × 10^{-4} molar solutions of the acids and ethyl esters (Table III).

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POTENTIOMETRIC AND VOLUMETRIC ESTIMATION OF PEROXIDES WITH ALKALINE PERMANGANATE

By I. M. Issa and H. Khalifa

Peroxide solutions reduce alkaline permanganate in presence of telluric acid to quadrivalent manganese. The method can be used for the potentiometric estimation of peroxides, the errors differing from the acid permanganate method by not more than 0.5%. Another method, which can be applied, consists in mixing the peroxide solution with excess of $KMnO_4$, in presence of 0.5 *N*-NaOH, and 0.2 g. telluric acid, followed by determining the excess oxidant with oxalic acid or ferrous iron.

In the current methods for analysing per-compounds, these are usually converted into hydrogen peroxide through the action of acids whereby the liberated hydrogen peroxide is titrated with a standard permanganate solution. In this investigation it is aimed to determine the peroxide solution by oxidation with alkaline permanganate Because of the instability of H_2O_2 in alkaline solutions, direct titration of peroxide solution is unsuccessful (Issa and Issa, *Anal. Chim. Acta*, under publication). The procedures followed here consist then in (*a*) titration of alkaline permanganate solutions with peroxide solutions and (*b*) mixing the peroxide solution with excess of $KMnO_4$, followed by estimating the excess oxidant with a suitable reductant.

Experimental

The peroxide solution (0.1-0.05 *N*) was prepared by dissolving either barium or sodium peroxide in 0.2-0.4*N*-HCl. The peroxide content was estimated by titration with permanganate in presence of H_2SO_4 and solid manganous sulphate. 0.1 *N*-$KMnO_4$ solution was prepared and standardised by the method of Stamm (*Z. angew. Chem.*, 1934, **47**, 791).

Procedures

(*A*). $KMnO_4$ solution (10-25 c.c.) was mixed with 5 *N*-NaOH to make the solution 0.5 to 1 *N* with respect to the alkali hydroxide. Telluric acid (0.2 g.) was then added, the solution well mixed and then titrated with the peroxide solution. The end-point was determined potentiometrically. The apparatus used was similar to that previously described (this *Journal*, 1955, **32**, 23). The peroxide solution was added dropwise on the permanganate-alkali mixture while continuously stirring the latter. The equilibria were rapidly attained except in the region of the end-point when usually 5-10 minutes were required.

TABLE I

Titration of permanganate in 1 *N*-NaOH *in presence of telluric acid.*
Vol. of $KMnO_4$ soln. taken = 10 c.c.

Titrant.	Conc. of $KMnO_4$.	Max. inflec. per 0.1 c.c. titrant.	End-point obs.	End-point calc.	% Error.
0.0543*N*-BaO_2 in 0.1*N*-HCl	0.1099 *N*	192 mv	12.08	12.11	0.25
0.0271*N*-BaO_2 in 0.05*N*-HCl	0.05495	150	12.09	12.14	0.41
0.0945*N*-Na_2O_2 in 0.2*N*-HCl	0.1099	222	6.99	6.98	0.15
0.0471*N*-Na_2O_2 in 0.2*N*-HCl	0.1099	212	13.98	14.00	0.14
0.09432*N*-Na_2O_2 in 0.2*N*-H_2SO_4 Alkalinity = 1.5*N*-NaOH.	0.1099	242	6.97	6.99	0.28

(*B*). This procedure involved mixing varying portions of 0.05 *N*-$KMnO_4$ solution with 0.2 g. of telluric acid ; it was then made 0.5 *N* with respect to NaOH. This was followed by a known volume of the peroxide solution while continuously shaking the mixture in a 100 c.c. Erlenmeyer flask. The solution was then transferred quantitatively to another 250 c.c. flask containing either a mixture of a known excess of an ice-cold mixture of 0.1108 *N* oxalic acid or 0.1204 *N* ferrous iron solution together with 20 c.c. of 4 *N*-H_2SO_4. After well mixing, the excess oxalic acid or ferrous iron was titrated with a standard permanganate solution. Table II contains typical data obtained by the above procedure.

TABLE II

$KMnO_4$ = 0.05495 *N*. Na_2O_2 = 0.0344 *N*. Oxalic acid = 0.1108 *N*.
Ferrous am. sulphate = 0.10204 *N*.

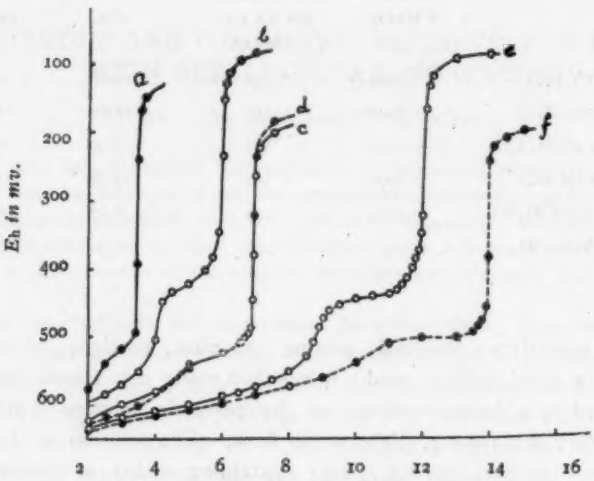
Volume of $KMnO_4$.	Volume of Na_2O_2.	Volume of Oxalic acid	Potassium permanganate equivalent to Excess oxalic or ferrous.	Potassium permanganate equivalent to Na_2O_2.	10 c.c. Na_2O_2. Visulal.	10 c.c. Na_2O_2. New procedure.	%Error.
10 c.c.	4 c.c.	10 c.c.	12.68 c.c.	2.51 c.c.	6.26 c.c.	6.28 c.c.	0.32
20	5	10	3.30	3.13	6.26	6.26	0.0
25	10	10	1.43	6.26	6.26	6.26	0.0
		ferrous.					
10	4	10	11.09	2.52	6.26	6.30	0.64
20	9	10	4.24	5.57	6.26	6 30	0.64

All solutions were made 0.5 *N* wfth respect to NaOH after addition of telluric acid.

DISCUSSION

The titration curves of permanganate with the peroxide solutions, as shown in Fig. 1, are characterised by the inflections each. The first inflection is not very

FIG. 1



Peroxide soln. added in c.c.

a—10 c c.	0.05495 *N*	× 0.0299 *N*-Na_2O_2	in 0.05 *N*-H_2SO_4
b—10	0.04595	× 0.0543	BaO_2 in 0.1 *N*-HCl
c—10	0.1099	× 0.0945	Na_2O_2 in 0.2 *N*-HCl
d—10	0.1099	× 0.0943	Na_2O_2 in 0.2 *N*-H_2SO_4
e—10	0.1099	× 0.0543	BaO_2 in 0.1 *N*-HCl
f—10	0.05495	× 0 0942	Na_2O_2 in 0.2 *N*-HCl

sharp and corresponds probably to reduction of permanganate to manganate. However, this inflection occurs always later than the theoretical value. The second inflection is quite sharp, amounting in the average to ~200 mv, and corresponds to the reduction of the higher oxidation state of manganese to Mn^{4+}. It is interesting to remark that the first inflection is sharper in the case of barium peroxide solution than with sodium peroxide, but even then occurs later than that corresponding to theory. This is most probably due to the partial reduction of $KMnO_4$ to MnO_2. At the second inflection it is found that despite the presence of Ba^{2+} ions, reduction passes completely to MnO_2, indicating that H_2O_2 can reduce the $BaMnO_4$, originally precipitated. The volume of peroxide consumed till this inflection coincides fairly well with the theoretical values with a maximum error of 0.5% (cf. Table I). The data shown in Table II, which are obtained by procedure (B), are also in good agreement with the acid permanganate method with a maximum error of 0.5%.

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FORMATION OF OXYGEN COMPLEXES ON CHARCOAL

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Surface oxygen complexes on charcoal come into existence during or within a few minutes of the formation of the charcoal, and extend themselves rapidly on exposure to oxygen but, gradually on exposure to air, to the same limiting value. The presence of moisture has no effect. Ageing in limited supplies of air produces slow and restricted effects. The amount of complex decomposing into CO_2 decreases with increase in the carbonisation temperature, while that decomposing into CO appears to be more or less independent of the carbonisation temperature. The base-neutralising capacity of charcoal is almost equivalent to the amount of CO_2 evolved on degassing the same at 1000°.

It is well known that almost all types of charcoals and activated carbons are covered by oxygen complexes (Lowry and Hulett, *J. Amer. Chem. Soc.*, 1920, **42**, 1408; Barrer, *J. Chem. Soc.*, 1936, 1261; Dewey and Lefforge, *Ind. Eng. Chem.*, 1932, **24**, 1045; Lawson, *Trans. Faraday Soc.*, 1936, **32**, 473; Anderson and Emmett, *J. Phys. Chem.*, 1947, **51**, 1308), the nature and composition of which vary with the treatment given to the sample (Schilow *et al.*, *Z. physikal. Chem.*, 1930, **149A**, 211; **150A**, 31; King, *J. Chem. Soc.*, 1937, 1489; Lepin, *Physikal. Z. Sowjetunion*, 1933, **4**, 282). The influence of these complexes on the adsorption of vapours, acids and bases has formed the subject matter of several publications (King and Lawson, *Trans. Faraday Soc.*, 1934, **30**, 1094; Dubinin and Zaverina, *J. Phys. Chem. U.S.S.R.*, 1947, **21**, 1373; McDermot and Arnell, *J. Phys. Chem.*, 1954, **58**, 492; Weller and Young, *J. Amer. Chem. Soc.*, 1948, **70**, 4155; Bruns *et al.*, *Kolloid Z.*, 1933, **63**, 286). It is generally believed that these complexes increase the capacity of charcoal to take up vapours and alkalies but decrease its capacity to adsorb acids.

Lowry (*J. Amer. Chem. Soc.*, 1924, **46**, 824) has pointed out that oxygen is slowly picked up by charcoal 'irreversibly' even at the room temperature. The recent work of Puri *et al.* (*Soil Sci.*, 1953, **75**, 209) also indicates that oxygen complexes are formed on exposure of charcoal to air or oxygen at ordinary temperatures. It is of interest to know how far these complexes exist on charcoal at the time of its formation and how far do they extend on exposure (at room temperature) to oxygen and air under different conditions. The present work was undertaken with these objectives in view.

Experimental

Charcoals were prepared by carbonisation of pure recrystallised cane sugar and coconut shell at temperatures varying from 350° to 600° in a Pyrex glass vessel placed in a heat-lagged nichrome coil for uniform electrical heating. The current was controlled with a Variac transformer.

The time of heating for the carbonisation varied between 30 and 90 minutes depending upon the carbonisation temperature. The smaller the temperature, the longer was the time allowed. The charcoals were immediately transferred to wide trays

and allowed to cool. The time required for this purpose was 10 to 15 minutes. The samples were split into four different groups, each weighing about 15 g. They were allowed to age under different conditions. One group was sealed in half-pound bottles; the second, spread in wide trays, forming 1 cm. thick layers, was exposed to air in a closet in which no foreign vapour or fumes could enter, though the air in it was renewed occasionally; the third group, similarly spread, was exposed to air having 80% relative humidity; the fourth, similarly spread, was exposed to oxygen in a wide-base bottle which was first evacuated and then filled with oxygen at the atmospheric pressure, the gas being renewed occasionally.

A representative sample was withdrawn from each group after different intervals of time for the determination of acid and base adsorption capacity, as shown below.

Acid Adsorption.—A sample of charcoal (0.5 g.) was shaken with 0.1 *N*-HCl solution (100 c.c.) for about 48 hours after which decrease in concentration was determined by titrating an aliquot of the clear supernatant liquid against a standard alkali solution in the usual manner.

Base Adsorption.—A charcoal sample (0.5 g.) was shaken with 100 c.c. of 0.2 *N*-$Ba(OH)_2$ solution (100 c.c.) for about 48 hours and the decrease in concentration was determined by titrating 20 c.c. of the clear supernatant liquid against a decinormal acid solution. This method has been shown (Puri *et al.*, *loc. cit.*) to provide the miximum capacity of charcoal to neutralise alkalies.

Evacuation at 1000°.—The samples, which had been allowed to age in air and in closed bottles for a period of six months, were subjected to evacuation in a resistance tube furnace at 1000° and the gases evolved were analysed in the following sequence. Carbon dioxide was estimated by passing through a series of Erlenmeyer flasks containing a known amount of a standard barium hydroxide solution. Carbon monoxide and hydrogen in the rest of the gaseous mixture were estimated by exploding with a known excess of oxygen, followed by the measurement of contraction produced on cooling and on the introduction of potash solution.

The ultimate vacuum over charcoal on evacuation was of the order of 10^{-2} mm. of mercury.

The results of these experiments are shown in Tables I—IV. Acid adsorption by sugar charcoal as well as coconut shell charcoal was of the order of 20 m.e. per 100 g., which remained almost unchanged on ageing or on altering the temperature of carbonisation. These results therefore have not been included.

TABLE I

DISCUSSION

It is interesting to note, on reference to Tables III and IV, in the first instance, that the CO_2 equivalent of the alkali, neutralised by charcoal, is quite close to the amount of CO_2 evolved from it on high-temperature evacuation. This shows that the capacity of charcoal to neutralise alkalies is almost entirely due to the presence of CO_2 in the charcoal complexes. This view was confirmed by observing that the evacuated charcoals lost their base-neutralising capacity almost entirely. This is in conformity with the conclusions previously arrived at (Puri *et al.*, this *Journal*, 1955, **32**, 219).

TABLE I

Base-neutralising capacity of sugar charcoal prepared at different temperatures on ageing under different conditions.

Carbonisation temp.	Condition of ageing.	$Ba(OH)_2$ (m.e.) per 100 g. of charcoal neutralised after different intervals of time								
		Initial	15 mins.	45 mins.	90 mins.	3 hrs.	6 hrs.	12 hrs.	3 days.	2 months.	6 months.
350°	Free air	340.1	355.0	356.2	358.1	366.9	368.7	371.5	399.9	487.9	492.3
	Humid air		...	353.7	...	364.7	370.3	...	398.6	...	489.2
	Limited air		345.2	349.1	350.6	351.8	352.3	358.0	363.6	368.9	390.7
	Oxygen		395.5	436.1	468.3	479.1	493.8	492.3	494.1	493.9	495.5
400°	Free air	291.3	310.4	319.3	320.4	321.9	323.6	329.5	334.4	345.4	355.8
	Humid air		...	317.0	...	323.6	...	328.5	...	341.9	353.7
	Limited air		293.9	310.4	315.4	318.1	320.3	...	325.1	321.8	333.9
	Oxygen		314.3	328.7	350.0	355.8	358.6	357.9	359.0	358.3	358.2
500°	Free air	29.2	77.6	87.5	90.5	97.0	98.2	99.8	101.4	125.9	132.2
	Humid air		...	84.8	...	...	96.7	...	99.7	...	129.9
	Limited air		67.9	77.3	82.0	84.3	94.3	97.0	98.8	100.3	102.5
	Oxygen		103.0	121.6	126.7	129.6	129.7	...	130.0	129.8	129.9
600°	Free air	17.9	34.7	35.8	36.5	36.8	37.7	39.5	40.8	53.6	55.8
	Humid air		...	33.7	...	...	38.7	...	...	54.0	56.5
	Limited air		22.3	23.3	26.5	27.3	27.6	35.9	36.6	40.8	43.7
	Oxygen		41.3	43.6	48.5	51.3	53.4	54.0	54.9	55.2	55.3

TABLE II

Base-neutralising capacity of cocoanut shell charcoal prepared at different temperatures on ageing under different conditions.

Conditions of ageing.	$Ba(OH)_2$ (m.e) Initial.	neutralised after different intervals of time per 100 g. of charcol. 15 mins.	45 mins.	60 mins.	90 mins.	3 hrs.	6 hrs.	12 hrs.	3 days.	15 days.	2 months.	6 months.
		Carbonisation temp. = 350°.										
Free air		375.4	387.8	390.5	397.6	401.2	428.0	431.7	444 6	475.8	510.7	513.3
Humid air	371 8	...	386 7	...	395.4	...	...	433.2	...	474.6	...	514.7
Limited air		373.1	377.2	381.3	388.5	389.6	394.5	396.0	399.8	409.7	427.6	438.2
Oxygen		526 3	527.9	529.3	531.6	534.8	536.8	538.2	538.5	539.3	538 9	539 1
		Carbonisation temp. = 400°.										
Free air		235.4	243.8	246 4	...	247.7	249.0	253.3	263.4	292.8	336 3	357.8
Humid air	217.4	...	241.9	...	...	248.3	...	...	261 8	...	337.1	360.0
Limited air		222 7	226.4	224.3	228 5	230.7	231.4	233.4	237 4	249.8	258.7	267 3
Oxygen		356.6	372.8	387.2	393.5	397.0	401.8	402.3	401.6	404.3	403.9	404 4
		Carbonisation temp. = 500°.										
Free air		203.6	226.7	236.4	252.3	257.8	268.4	278.5	286.7	306.4	318.7	329.4
Humid air	197.4	...	225.4	...	...	258.0	...	277.3	...	...	319 4	328.7
Limited air		199.7	208.5	211.3	216.6	219.6	221 3	238.7	...	240.6	241.3	244 3
Oxygen		256.6	287.5	307.4	319.8	336.4	340.1	342.1	344.2	346.5	345.9	346.1

TABLE III

Degassing of different samples of sugar charcoal at 1000°.*

	Description of the samples.	CO_2 equiv. of the alkali, neutralised by charcoal (cf. Table I.) (c.c. N.T.P./g.)	Amounts of gases evolved on evacuating at 1000° (c.c. N.T.P./g.). CO_2.	CO.	H_2.
1.	Carbonised at 350° and exposed to free supply of air for 6 months.	55.13	55.33	92.35	101.98
2.	Do, but exposed to limited supply of air for 6 months.	43.76	41.97	83.53	98.04
3.	Carbonised at 400° and exposed to free supply of air for 6 months.	39.85	40.43	84.87	98.38
4.	Do, but exposed to limited supply of air for 6 months.	37.39	36.75	75.21	99.75
5.	Carbonised at 500° and exposed to free supply of air for 6 months	14.80	15.18	79.78	98 87
6.	Do, but exposed to limited supply of air for 6 months.	11.48	12.28	68.97	103.63
7.	Carbonised at 600° and exposed to free supply of air for 6 months.	6.25	6.72	80 13	102.43
8.	Do, but exposed to limited supply of air for 6 months.	4.89	5.02	69.89	98.43
9.	Carbonised by sulphuric acid and exposed to oxygen.	68.10	68 48	87 32	105 32

* The samples of sugar charcoal were almost free of ash.

TABLE IV

Degassing of different samples of coconut shell charcoal at 1000°.*

	Description of the samples.	CO_2 equiv. of the alkali, neutralised by charcoal (cf. Table II) (c.c. N.T.P./g.)	Amounts of gases evolved on evacuating at 1000°. (c.c. N.T.P./g.) CO_2.	CO.	H_2.
1.	Carbonised at 350° and exposed to free supply of air for 6 months.	57.50	54.29	77.95	83.25
2.	Do, but exposed to limited supply of air for 6 months.	49.08	47.37	69.71	81.98
3.	Carbonised at 400° and exposed to free supply of air for 6 months.	40.07	39.97	78.34	83.12
4.	Do, but exposed to limited supply of air for 6 months.	29.94	28.76	71.54	84.32
5.	Carbonised at 500° and exposed to free supply of air for 6 months.	36.89	37.34	76.76	78.06
6.	Do, but exposed to limited supply of air for 6 months.	27.36	25.65	70.86	83.21

* The samples were rendered ash-free before degassing.

Thus, increase in the base-adsorption capacity (b.a.c.) of charcoal on ageing, as shown in Tables I and II, may be attributed to increase in the amount of the CO_2-complex, and it may be inferred from these results (Tables I and II) that the surface oxidation of charcoal, leading to the formation of this complex, proceeds rapidly in oxygen, but only gradually in air. The change brought about by oxygen in six hours is almost the same as that brought about by air in about 6 months. The presence of moisture does not appear to have any effect on the rate of the amount of formation of the complex. However, if charcoal is allowed to age in a limited supply of air (as in closed bottles in the present experiments), surface oxidation takes place to a small extent only. It can be shown by simple calculations that oxygen contained in the air of the sealed bottles (half-pound capacity) is sufficient to bring about the small increase in the complex which has actually been observed to take place. Moreover, the botties had to be opened occasionally while withdrawing the samples.

It is also evident (Tables I and II) that it is not possible to increase b.a.c. of charcoal beyond a certain limit even on prolonged exposure to oxygen, which shows that the amount of CO_2- complex cannot increase beyond a certain maximum value on exposure to oxygen at ordinary temperatures.

Considering the rate of 'pick-up' of oxygen from free supply of air, it is seen that it is quite rapid to begin with, but it falls appreciably afterwards. It will be noted, for instance, that in several cases (Tables I and II) the value obtained after 12 hours' exposure to air, is as high as 70 to 80% of the maximum but in order to pick up the remaining 20 to 30% of the value, the samples have to be exposed to air for a period of about six months. It is also seen that even the 'initial' values are quite appreciable. It may be mentioned that these 'initial' values were actually determined on cooling charcoal to room temperature after its preparation at a particular temperature, and this naturally took a few minutes. The surface oxidation in the first few minutes therefore appears to be even more rapid.

The carbonisation temperature also seems to influence the formation of the CO_2-complex appreciably. As the temperature rises, the base-neutralising capacity, initial as well as ultimate, determined on exposure to air or oxygen, decreases. The amount of CO_2 evolved also decreases (Tables III and IV) with increase in the carbonisation temperature. The amount of CO evolved, however, appears to be more or less independent of the carbonisation temperature although it is more in free air than in limited air. It appears that the CO_2-complex, which is known to be less stable (Smith *et al.*, *J. Phys. Chem.*, 1954, **58**, 298; Puri *et al.*, *Punjab University Res. Bull.*, 1956), is decomposed to a certain extent with rise in the carbonisation temperature and is not reformed easily on simple exposure to air or oxygen at ordinary temperatures, but the CO-complex, which is much more stable (*loc. cit.*), remains more or less unchanged up to 600°, which is the maximum temperature employed for carbonisation in these experiments.

A small amount of sugar charcoal was also prepared by bringing about the carbonisation with concentrated sulphuric acid. The mass was washed repeatedly with distilled water to free it completely from the sulphate ions. The capacity of

this charcoal for neutralising barium hydroxide was 608 m.e./100 g. after exposure to oxygen. The sample on evacuation also afforded the corresponding amount of CO_2, as shown in Table III. It is evident that the amount of CO_2-complex formed now is much greater. Probably the average carbonisation temperature was even less than 350° in this case. However, it is interesting to note that the amount of CO evolved remains almost unchanged, as expected. It might be argued that the treatment with sulphuric acid itself probably adds more oxygen which is eliminated as CO_2. In order to verify this point, the samples carbonised at 350° and 400° were given similar treatments with sulphuric acid, followed by similar repeated washings with distilled water, but no increase in their base-neutralising capacities nor in the amount of gases evolved on evacuating at 1000° was noticed.

The results reported in Tables III and IV show incidentally that hydrogen also gets fixed up by charcoal to an appreciable extent and that this is given out in the free state on degassing at high temperatures. Its amount remains almost independent of the carbonisation temperature up to 600°. This is to be expected since hydrogen is known to be evolved from carbons in the temperature range of 900°-1200° (Anderson and Emmett, *J. Phys. Chem.*, 1947, **51**, 1308 ; 1952, **56**, 753 ; Puri *et al.*, *Chem. & Ind.*, 1956, *B. I. F. Review*, 30).

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HYDROXYKETONES. PART VI. THE FRIES REARRANGEMENT OF THE PHENOLIC ESTERS OF *o*- AND *m*-NITROBENZOIC ACIDS AND SOME THIOPHENYL ESTERS

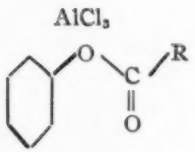
By G. S. Saharia and B. R. Sharma

The Fries migrations of *o*- and *m*-nitrobenzoic acid esters with phenol, isomeric cresols and naphthols have been studied. The esters of *m*-nitrobenzoic acid afforded normal migration products while the reaction failed with the esters of *o*-nitrobenzoic acid. This behaviour could be explained due to the absence of complex formation at the phenoxyl oxygen, which is sterically hindered.

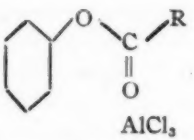
The migrations of thiophenyl acetate and benzoate were also tried, but without any success.

In continuation of our earlier work (Saharia and Sharma, *J. Sci. Ind. Res.*, 1955, **14B**, 263), the present communication deals with the Fries migrations of the esters of *o*- and *m*-nitrobenzoic acids with phenol, isomeric cresols and naphthols. The compounds thus prepared are expected to be bactericides.

The important observation made during the course of this study was that only the esters of *m*-nitrobenzoic acid furnished normal migration products while those of *o*-nitrobenzoic acid failed to rearrange. This difference is intelligible only if the mechanism of the Fries reaction is closely examined. The generally accepted view at present is that the reaction takes place through a complex formation of the type (I) (Dewar, "The Electronic Theory of Organic Chemistry", Oxford University Press, 1949, p. 230; Lunder and Zuffanti, "The Electronic Theory of Acids and Bases", John Wiley and Sons, New York, 1946, p. 123; Baltzly *et al.*, *J. Amer. Chem. Soc.*, 1948, **70**, 4192; 1955, **77**, 2522; Sharma, M.Sc. Thesis, Panjab University, 1954).



(I)



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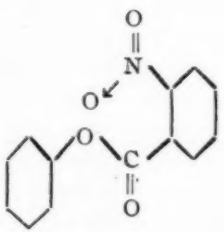

(III)

In the case of the esters of *o*-nitrobenzoic acid (III), a complex formation of the type (I) is hindered by the nitro group which overshadows the phenoxyl oxygen atom, while with the esters of *m*- and *p*-nitrobenzoic acids no such hindrance is possible as normal migration products have been isolated in the latter cases.

Table I

[NB denotes *m*-nitrobenzoate]

	Ester.	M.P.	Cryst. shape.	Solvent.	Yield.	Formula.	% Carbon. Found.	% Carbon. Calc.	% Hydrogen. Found.	% Hydrogen. Calc.
A.	Phenyl-NB	100°	Colorless prisms.	Dilute alcohol.	63%	$C_{13}H_9O_4N$	64.1	64.2	3.6	3.7
B.	*p*-Cresyl-NB	78°	Shining colorless leaflets.	Alcohol.	66	$C_{14}H_{11}O_4N$	65.2	65.4	4.5	4.3
C.	*m*-Cresyl-NB	68°	Colorless plates.	,,	70	$C_{14}H_{11}O_4N$	65.3	65.4	4.2	4.3
D.	*o*-Cresyl-NB	101-102°	Colorless prisms.	Dilute alcohol	64	$C_{14}H_{11}O_4N$	65.1	65.4	4.2	4.3
E.	α Naphthyl-NB	109°	Colorless plates.	Alcohol-acetone.	63	$C_{17}H_{11}O_4N$	70.0	69.6	3.5	3.8
F.	β-Naphthyl-NB	138° (Lit. 134°)	Light brown shining leaflets.	,,	80	$C_{17}H_{11}O_4N$	...	...	...	...

Table II

[N- denotes 3′-nitrobenzophenone]

*	Ester.	Ketone.	M.P.	Cryst. shape.	Solvent.	Yield.	Formula.	% Carbon. Found.	% Carbon. Calc.	% Hydrogen. Found.	% Hydrogen. Calc.	2:4-Dinitrophenyl hydrazone m.p.
A.	(a)	4-Hydroxy-N	173°	Colorless needles.	Dilute alcohol.	32.5%	$C_{13}H_9O_4N$	...	...	...	...	210°
	(b)	2-Hydroxy-N	101° (lit. 173°)	Yellow needles.	Pet. ether (60°-80°)	5.0	$C_{13}H_9O_4N$	64.0	64.2	3.9	3.7	238-9°
B.		2-Hydroxy-5-methyl-N	104-105°	Bright yellow leaflets.	Dilute alcohol.	62.5	$C_{14}H_{11}O_4N$	65.2	65.4	4.5	4.3	226°
C.	(a)	2-Methyl-4-hydroxy-N	200°	Dark brown needles.	Benzene.	10.0	,,	65.5	65.4	4.4	4.3	—
	(b)	2-Hydroxy-4-methyl-N	132°	Bright yellow needles.	Pet. ether (50°-80°)	15.0	,,	65.5	65.4	4.2	4.3	248-9°
D.	(a)	3-Methyl-4-hydroxy-N	182-83°	Tiny colorless needles.	Dilute alcohol.	15.0	,,	65.2	65.4	4.2	4.3	233-4°
	(b)	2-Hydroxy-3-methyl-N	115°	Bright yellow needles.	Pet. ether (60°-80°)	7.5	,,	65.2	65.4	4.4	4.3	—
E.		1-Hydroxynaphthyl (2)-3′-nitrophenyl ketone	168°	,,	,,	20.0	$C_{17}H_{11}O_4N$	69.6	69.6	4.0	3.8	284°
F.		2-Hydroxynaphthyl-(1)-3′-nitrophenyl ketone	160°	Shining yellow plates.	Pet. ether (60°-80°) and benzene.	25.0	,,	69.4	69.6	3.8	3.8	—

* Vide Table I

If the complex formation of the type (II), as advocated by other workers (Ralston *et al.*, *J. Org. Chem.*, 1940, **5**, 645, 2169; 1941, **6**, 751; Amin and Shah, *J. Univ. Bombay*, 1948, **17**, Part III, 352; Illare, *Gazzetta*, 1948, **77**, 339, 352), is important for the rearrangement, the esters of the type (III) should have furnished the normal reaction products. In absence of any such products the importance of the complex formation (if any) for the Fries reaction at the carbonyl oxygen atom is completely ruled out.

The experimental procedure adopted for the preparation of the esters, their migrations and working up of the products was similar to the one followed earlier (Saharia and Sharma, *loc. cit.*).

In the case of the esters of *o*-nitrobenzoic acid, though varied reaction conditions, such as the use of different solvents, temperatures and quantities of aluminium chloride, were employed, the desired products could not be obtained. The esters were recovered unchanged at lower temperatures while at higher temperatures the reaction mixture became charred.

Keeping in view the acid-base relationship of aluminium chloride and ester in the Fries reaction, it was proposed to study the migrations of thiophenolic esters. Accordingly, thiophenyl acetate and benzoate were prepared and subjected to the Fries reaction, but it did not proceed; most of the ester was recovered unchanged, while a considerable portion got decomposed (cf. Tarbell *et al.*, *J. Amer. Chem. Soc.*, 1953, **75**, 1668). This difference in behaviour could only be explained on the basis that the sulphur atom has got a larger atomic volume, and hence, a loose control on its valency electrons. It is possible that aluminium chloride forms a complex with the sulphur atom, yet it may not be strong enough to detach the carbonium ion ($R.\overset{+}{C}O$) to afford the rearranged products.

Experimental

Preparation of o- *and* m-*Nitrobenzoic Acid Esters*.—The acid chloride (Vogel, "Practical Organic Chemistry", Longman Green & Co., New York, 1948, p. 751) (1*M*) and the phenols (1 *M*) were thoroughly mixed by shaking in alkaline medium and cooled. The solid esters so obtained were crystallised.

Fries Rearrangement.—The ester (1 *M*) was intimately mixed with $AlCl_3$ (anhyd., 1.3 *M*) in a round-bottomed flask (100 c.c.) fitted with a guard tube and the reaction was carried out at 120° and 160° in an oil-bath for 2 hours. The reaction product was hydrolysed with crushed ice and HCl (dil.) and then extracted with ether. The ethereal solution was washed free of any acid and then extracted with sodium carbonate (5%) and sodium hydroxide (2%), which on acidification deposited the *para* and *ortho*-hydroxyketones respectively. The residual ethereal solution was worked up for any unchanged ester.

The *o*-hydroxyketones developed violet or dark red coloration with ferric chloride. The ketones were characterised through their 2:4-dinitrophenylhydrazones. The esters and the ketones are described in Tables I and II.

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CHEMISTRY OF BERYLLIUM. PART I. FORMATION OF BERYLLATES

By Sarju Prasad and Kashi Prasad Srivastava

The formation of calcium, strontium, barium, magnesium, zinc, cobalt and nickel beryllates has been studied at high temperatures and the following compounds have been obtained: CaO.3BeO, 2CaO.3BeO; SrO.3BeO, 2SrO.3BeO, SrO.BeO; BaO.3BeO; 2BaO.3BeO, BaO.BeO; MgO.3BeO; ZnO.3BeO; CoO.BeO; NiO.BeO.

Kruss and Morhat (*Annalen*, 1890, **260**, 173) obtained $Na_2O.BeO$ and $K_2O.BeO$, which on analysis afforded high results for Na and K than what theoretically required. Matignon and Marchal (*Compt. rend.*, 1927, **184**, 715) observed that when heated with beryllium metal, MgO and KOH were completely reduced at 1280° and 700° respectively, barium and aluminium oxides were partly reduced at 1230° and 1280° respectively, whilst lime formed a suboxide of calcium at 1230°-1280°. They further observed (*ibid.*, 1927, **185**, 812) that beryllia was reduced to the metallic state when heated in vacuum with excess of lime at about 800°, magnesia at 675°- 690° for three hours, and alumina at 1270° for four hours. When fluxes were used with the reaction mixture containing lime or magnesia, the yield of beryllium increased.

Lang *et al.* (*J. Res. Nat. Bur. Standards*, 1952, **48**, 298) studied the phase equilibria of the system $BeO\text{-}Al_2O_3$ at high temperatures and observed the eutectics

(*i*) at 1890° ± 10°; mol. ratio, 1 BeO : $4Al_2O_3$

(*ii*) at 1850° ± 10°; mol. ratio, 2 BeO : $3Al_2O_3$

(*iii*) at 1835° ± 10°; two congruently melting compounds BeO. $3\ Al_2O_3$ at 1910° ± 10° and $BeO.Al_2O_3$ at 1870° ± 10°.

Preliminary experiments were carried out to prepare beryllates by treating the solutions of sodium or potassium beryllates with solutions of soluble salts of other elements, but in no case a pure compound could be isolated.

The present investigation was therefore undertaken with a view to studying the formation of beryllates of alkaline earth metals, Zn, Ni and Co at high temperatures.

Experimental

As acids of different concentrations were used for the extraction of the reaction products, the solubility of BeO, ignited at high temperatures, in acids was studied under different experimental conditions. The results are shown in Table I.

Several mixtures were prepared by weighing out accurately beryllium oxide and the other constituent in different proportions. These were mixed separately in agate pestle and mortar, transferred into fire-clay or graphite crucibles and heated at high temperatures for different intervals of time. Duplicate experiments were carried out in each case and the results reported in the following tables are an average of the two values. The heated mass was taken out, powdered well, and weighed. A known weight of this mixture was taken for analysis. It was washed free of the unchanegd oxides ; CaO with 10% glycerine solution and finally with CO_2-free water ; SrO and BaO with hot CO_2-free water ; ZnO with hot 10% NH_4Cl solution ; MgO with 1*N*-HCl ; NiO with 2*N*-, 5*N*-HCl and finally with 5% NH_4OH ; CoO with 2*N*- and 5*N*-HCl. The residue was then extracted with a measured volume of 2*N*-HCl, 5*N*-HCl or HCl (conc.) and the quantity of beryllium and the other constituents estimated by standard methods in the acid extracts. The chemicals used in the following experiments were of Merck's C.P. quality or B.D.H. Laboratory reagents.

TABLE I

Solubility of heated beryllium oxide at diff. temp. in diff. intervals of time.

Time of heating = 2.0 hours.

Expt. No.	Acid used.	BeO	BeO heated at	Time.	Temp.	BeO dissolved/100 c.c. of acid.
1	2*N*-HCl	0.2218 g.	1000°-1050°	5 mins.	25°	0.0032 g.
2	,, ,,	0.2196	,, ,,	1 hr.	,,	0.0060
3	5*N*-HCl	0.2726	,, ,,	5 mins.	,,	0.0100
4	,, ,,	0.2950	,, ,,	1 hr.	,,	0.0272
5	2*N*-HCl	0.3152	1100°-1150°	5 mins.	,,	0.0012
6	,, ,,	0.3140	,, ,,	1 hr.	,,	0.0020
7	5*N*-HCl	0.2854	,, ,,	5 mins.	,,	0.0048
8	,, ,,	0 2806	,, ,,	1 hr.	,,	0 0104
9	,, ,,	0.3100	1350°-1400°	2 hrs.	,,	0.0000
10	,, ,,	0.3100	,, ,,	12 hrs.	,,	0.0284
11	,, ,,	0.2958	,, ,,	1 hr	100°	0.0456
12	5*N*-HNO_3	0.4854	,, ,,	2 hrs.	25°	0.0000
13	,, ,,	0.4854	,, ,,	12 hrs.	,,	0.0282
14	,, ,,	0.4714	,, ,,	1 hr.	100°	0.0332

TABLE II

Calcium beryliates.

Time of heating = 2.0 hours. Temp. = 1000°-1050°.

Expt. No.	BeO.	$Ca(OH)_2$.	$CaCl_2$.	Acid (2*N*-HCl)-soluble CaO.	Acid (2*N*-HCl)-soluble BeO.	Compound.
1	0.5 g.	1.5 g.	...	0.2995 g.	0.2095 g.	2CaO.3BeO
2	,,	3.0	...	0.0570	0.0404	2CaO.3BeO
3	,,	4.5	...	0.0502	0.0350	2CaO.3BeO
4	1.0	3.0	3.0 g.	0.4934	0.6526	CaO.3BeO
5	1.0	2.0	4.0	0.2255	0.2766	CaO.3BeO
6	1.0	5.0	10.0	...	...	... ...

TABLE III

Strontium beryllates.

Time of heating = 2.0 hours.

Expt. No.	BeO.	$Sr(OH)_2$	Compound added.	Temp.	Acid (2*N*-HCl)-soluble. SrO.	BeO.	Compound.
7	0.5 g.	6.0 g.	...	1000°-1050°	0.3819 g.	0.2838 g.	SrO.3BeO
8	0.5	6.0	...	1100°-1150°	0.8490	0.3072	2SrO.3BeO
9	0.5	12.0	...	,, ,,	1.8044	0.4370	SrO.BeO
10	1.0	6.0	$SrCl_2$ 6.0 g.	1000°-1050°	1.1152	0.7312	SrO.3BeO
11	1.0	6.0	$SrCl_2$ 10.0	,, ,,	0.8052	0.6044	SrO.3BeO
12	0.5	...	$Sr(NO_3)_2$, $4H_2O$ 6.0	1100°-1150°	1.0288	0.3680	2SrO.3BeO

TABLE IV

Barium beryllates.

Time of heating = 2.0 hours.

Expt. No.	BeO.	$Ba(OH)_2$.	$BaCl_2,2H_2O$.	Temp.	Acid (2*N*-HCl)-so'uble. BaO	BeO	Compound.
13	0.5 g.	4.0 g.	...	1000°-1050°	0.3131 g.	0.1524 g.	BaO.3BeO
14	0.5	2.0	...	1100°-1150°	0.4503	0.1129	2BaO.3BeO
15	0.5	4.0	...	,, ,,	1.2178	0.3076	2BaO.3BeO
16	0.5	8.0	...	,, ,,	1.6230	0.3585	2BaO.3BeO
17	0.5	16.0	...	,, ,,	2.3532	0.3872	BaO.BeO
18	1.0	10.0	10.0 g.	1000°-1050°	1.1436	0.5616	BaO.3BeO
19	1.0	10.0	15.0	,, ,,	1.0245	0.5024	BaO.3BeO

TABLE V

Magnesium, zinc, cobalt and nickel beryllates.

Time of heating = 4 hours.

Expt. No.	BeO.	Compound added.		Temp.	Conc. of HCl.	Acid-soluble. Metal oxide.	BeO.	Compound.
20	2.00	$MgCO_3$	2.00 g.	1350°-1400°	5*N*	Traces	Traces	... ...
21	2.00	,, ,,	4.00	,, ,,	,,	0.3130 g.	0.6190 g.	MgO.3BeO
22	2.00	,, ,,	8.00	,, ,,	,,	0.4780	0.8640	MgO.3BeO
23	2.00	,, ,,	10.00	,, ,,	,,	0.7745	1.4554	MgO.3BeO
24	2.00	ZnO	6.00	,, ,,	2*N*	0.3262	0.3162	ZnO.3BeO
25	2.00	,, ,,	12.00	,, ,,	,,	0.4891	0.4758	ZnO.3BeO
26	2.00	,, ,,	20.00	,, ,,	,,	0.8343	0.7574	ZnO.3BeO
27	1.00	$NiCl_2$	7.00	1000°-1050°	10-12*N*	2.4255	0.7040	NiO.BeO
28	1.00	,, ,,	10.00	,, ,,	,,	1.9564	0.5632	NiO.BeO
29	2.00	Co-oxalate	20.00	1350°-1400°	,,	3.2460	1.3563	CoO.BeO
30	2.00	,, ,,	25.00	,, ,,	,,	3.8010	1.4558	CoO.BeO
31	1.00	$CoCl_2$	12.00	1000°-1050°	,,	2.0712	0.6250	CoO.BeO
32	1.00	,, ,,	20.00	,, ,,	,,	1.9880	0.5520	CoO.BeO

Discussion

Since BeO is more basic than Al_2O_3, the beryllates formed in solutions are generally unstable, and $Be(OH)_2$ precipitates out either on dilution or on heating. Some beryllates are, however, formed at high temperatures and are stable. Some of these are not decomposed even when heated with HCl (conc.).

Calcium, Strontium and Barium Beryllates

When mixtures containing BeO and hydroxide of calcium, strontium or barium in varying proportions are heated at high temperatures, different beryllates are formed. Their composition depends on the proportion of the constituents in the mixtures and the temperature at which the reaction is carried out.

It is interesting to note that when respective chlorides are added to the mixture, the compound XO. 3BeO (X = Ca, Sr or Ba) is formed in all the cases. The addition of chlorides seems to effect the reaction in two ways: (*i*) It makes the mass homogeneous and therefore the reaction proceeds to a greater extent than in their absence, and (*ii*) the reaction, $XCl_2 + BeO = BeCl_2 + XO$, starts at the m.p. of the chlorides, as has already been observed by Booth and Marshall (U.S. Pat. 1392015, 1392046) and $BeCl_2$ formed volatilises away.

In Expts. No. 4, 5 and 6 the quantity of the beryllates formed decreases as the quantity of $CaCl_2$ added is increased so that in Expt. No. 6, when the ratio of $BeO : CaCl_2$ is 1 : 10, no beryllate is obtained. $CaCl_2$ melts at 780° and considerable time is taken to reach 1000° at which the oxides react to furnish the beryllates. During this period $BeCl_2$ formed keeps on volatilising away, and by the time the furnace attains the temperature of over 1000°, no BeO is left to react with calcium oxide.

Similar results were obtained when $SrCl_2$ and $BaCl_2.2H_2O$ were added to the reaction mixtures, though the reaction (*ii*) was not so marked.

Calcium Beryllates.—It is evident from the Expts. No. 1, 2 and 3 that when mixtures containing BeO and $Ca(OH)_2$ in the ratio of 1 : 3, 1 : 6 and 1 : 9 are heated at 1000°-1050°, the compound 2CaO.3BeO is formed in all the cases, the quantity of the beryllate formed, however, decreases as the quantity of calcium hydroxide is increased.

Strontium Beryllates.—Expts. No. 7-12 show that strontium forms three beryllates: SrO. 3BeO, 2SrO 3BeO and SrO.BeO. Mixtures containing BeO and strontium hydroxide in the ratio of 1 : 12, when heated, afforded SrO. 3BeO at 1000°-1050° (Expt. No. 7) and 2SrO.3BeO at 1100°-1150° (Expt. No. 8). This compound was also formed when BeO and strontium nitrate in the ratio of 1 : 12 were heated together at 1100°-1150° (Expt. No. 12). It is interesting to note that when mixtures containing BeO and strontium hydroxide in the ratio of 1 : 24 are heated at 1100°-1150°, the compound SrO BeO is obtained.

Barium Beryllates.—Barium also forms three beryllates: BaO. 3BeO, 2BaO.3BeO and BaO.BeO. In Expts. No. 13, when BeO and barium hydroxide in the ratio 1 : 8 were

heated together at 1000°-1050°, BaO. 3BeO was formed. In Expts. No. 14-17, four different mixtures containing BeO and barium hydroxide in the ratio of 1:4, 1:8, 1:16, 1:32 were heated at 1100°-1150. In the first three cases, a white mass, which disintegrated easily when boiled with water, was obtained. This on analysis has been found to be 2BaO. 3BeO. However, in the last case a hard greenish mass was formed which on analysis showed the formation of the compound BaO. BeO.

Magnesium, Zinc, Cobalt and Nickel Beryllates

When mixtures containing varying proportions of $MgCO_3$ and BeO, ZnO and BeO, NiO and BeO and cobalt oxalate and BeO were heated at 1000°-1050° and 1100°-1150°, no beryllate was formed in any case.

Magnesium, Beryllate.—Four different mixtures containing BeO and $MgCO_3$ in the ratio of 1:1, 1:2, 1:4 and 1:5 were heated at 1350°-1400° for four hours. A very small quantity of the acid-soluble compound was formed in the first case but MgO. 3BeO was formed in the last three cases. It is interesting to note that the quantity of the beryllate formed increases considerably as the quantity of $MgCO_3$ is increased. No beryllate was formed at 1000°-1050° on addition of $MgCl_2$ or K_2SO_4.

Zinc Beryllate.—In Expts. No. 24, 25 and 26, when mixtures containing BeO and ZnO in ratios of 1:3, 1:6 and 1:10 were heated at 1350°-1400°, the compound ZnO.3BeO was obtained in each case. When K_2SO_4 was added to the reaction mixture, no beryllate was formed at 1000°-1050°.

Cobalt Beryllate.—In Expt. No. 29 and 30, two mixtures containing BeO and cobalt oxalate in the ratios of 1:10 and 1:12.5 were heated at 1350°-1400°, when a dark blue crystalline mass was obtained. After dissolving the free cobalt oxide in 5*N*-HCl, the residue was boiled with HCl (10-12*N*) several times and filtered. The ratio of cobalt oxide and BeO in the filtrate shows the compound to be CoO. BeO. The residue was fused with Na_2CO_3 and KNO_3 and extracted with HCl. On analysis this also has proved to be CoO.BeO, showing thereby that the total quantity of BeO has been acted upon by CoO.

The compound CoO.BeO is also formed when BeO and cobalt chloride in varying proportions are heated at 1000°-1050°, but the compound formed is a dark blue, amorphous powder in this case.

Nickel Beryllate.—It is interesting to note that NiO and BeO do not react even at 1350°-1400°, but when mixtures containing BeO and nickel chloride in varying proportions are heated at 1000°-1050°, a greenish mass is obtained, which on analysis is found to be the compound NiO.BeO.

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CONDENSATION PRODUCTS OF BENZYLIDENE-ACETONE WITH SUBSTITUTED THIOUREAS

By M. K. Rout

Several 2-arylamino-4-styryl-thiazoles, prepared by condensation of benzylidene-acetone with substituted thioureas, and their mercurated products have been described. Their bactericidal and fungicidal properties have also been evaluated with a view to examining the effect of styryl group in 4-position of the thiazole nucleus.

In continuation of our investigations on secondary thiazolyl amines and their mercurated products (Pujari and Rout, *J. Amer. Chem. Soc.*, 1953 **75**, 4057 ; this *Journal*, 1954, **31**, 257 ; Mahapatra and Rout, *ibid.*, 1953, **30**, 398), the present work describes several 2-arylaminothiazoles having a styryl group in 4-position of the thiazole nucleus. They were prepared by the reaction of benzylidene-acetone with substituted thioureas by the modified method of Rout and Pujari (*loc. cit.*).

Bactericidal and fungicidal activities of the above compounds have been investigated as secondary and tertiary thiazolyl amines themselves are reported to be of considerable therapeutic and biological importance (Erlenmeyer and Muller, *Helv. Chim. Acta*, 1945, **28**, 922 ; Sondern and Breivogel, U.S. Pat. 2,440,730, May, 1948) and some thiazole compounds like Asterol dihydrochloride or 2-mercaptobenzothiazole are well-known fungicides. 2-Arylamino-4 : 5-dimethylthiazoles have also been reported by Das, Padhi and Rout (*Nature*, 1954, **174**, 516) to possess appreciable fungicidal action.

A study of bactericidal and fungicidal activities of these compounds renders possible evaluation of the effect on these activities of a styryl group in 4-position of the thiazole nucleus and also that of different aryl substituents on the amino group.

Consistent with our earlier findings (this *Journal*, 1954, **31**, 357), mercuration with mercuric acetate gives rise to 2-(acetoxymercuri-arylamino)-4-styryl-thiazoles.

Experimental

4-Styryl-2-phenylaminothiazole.—To a mixture of benzylidene-acetone (2.92 g.), phenylthiourea (6 g.) and iodine (5.08 g.) benzene (15 c.c.) was added and the whole heated on a water-bath for about 16 hours. Excess of iodine was removed, the crude product was boiled with water and the hot water extract decanted off. To the residual gummy mass liquor ammonia was added and left overnight. The gum solidified. It was filtered and the solid was crystallised from alcohol, m.p. 83°, yield 64%. (Found : N, 9.8 ; S 11.2. $C_{17}H_{14}N_2S$ requires N, 10.07 ; S, 11.5 per cent).

Mercuration of Thiazoles.—A solution of the compound (1 *M*) in alcohol-acetic acid mixture was added to mercuric acetate (1.3 *M*), dissolved in water (15 to 20 c.c.) containing 2 or 3 drops of acetic acid. The stirring was continued for about 15 minutes and then left overnight with occasional stirring. It was filtered and purified by repeated washing with hot water and very dilute acetic acid.

TABLE I

Comp. No.	Aryl group.	4-Styryl-9-arylaminothiazoles. M.P.	Yield.	% Nitrogen. Found.	% Nitrogen. Calc.	% Sulphur. Found.	% Sulphur. Calc.	Comp. No.	4-Styryl-2-(acetoxymercuri)-arylaminothiazoles. M.P.	Yield.	% Mercury Found.	% Mercury Calc.
1	Phenyl	83°	64%	9.8	10.07	11.2	11.5	13	196°	69%	37.1	37.3
2	*o*-Tolyl	85°	68	9.2	9.59	10.8	10.95	14	159°	71	35.8	36.2
3	*p*-Tolyl	170°	65	9.1	9.59	10.6	10.95	15	170°	70	35.9	36.2
4	*o*-Chlorophenyl	77°	73	8.7	8.92	10.1	10.2	16	160°	75	35.2	35.3
5	*m*-Chlorophenyl	105°	75	8.6	8.92	10.35	10.2	17	164°	73	34.9	35.3
6	*p*-Chlorophenyl	86°	76	8.55	8.92	10.3	10.2	18	158°	72	34.8	35.3
7	*o*-Carboxyphenyl	265°	65	8.60	8.69	10.07	9.94	19	228°	64	34.1	34.5
8	*p*-Carboxyphenyl	175°	60	8.30	8.69	9.5	9.94	20	208°	65	34.2	34.5
9	*m*-Nitrophenyl	89°	75	8.51	8.67	10.6	9.9	21	220°	73	34.0	34.4
10	*p*-Nitrophenyl	170°	73	8.45	8.67	10.1	9.9	22	198°	70	34.1	34.4
11	α-Naphthyl	144°	71	8.32	8.54	9.5	9.7	23	206°	75	33.5	34.1
12	β-Naphthyl	140°	74	8.16	8.54	9.1	9.7	24	195°	78	33.9	34.1

Bactericidal Activity.—The Rideal-Walker drop serial dilution method was used for the study of the comparative antibacterial action. The results of biological tests indicating the maximum effective dilution (M.E.D.) of the compounds at 10 minutes' contact are shown against the compounds in Table II. The temperature was 36°. The test organisms were 24 hours' culture of both gram-positive and gram-negative organisms such as *E. Coli* and *Staphylococcus aureus*.

Fungicidal Tests.—For fungicidal assay, the method of Montgomery and Moore (*J. Pomol. Hort. Sci.*, 1938, **25**, 253) with slight modifications has been used. *Alternaria Polanduii* Ayyangar was used as the fungus indicator. All the mercurated and unmercurated thiazoles have been tested. The dilution at which spore germination takes place inspite of the presence of the test material and the percentage of germination corresponding to that dilution are recorded in Table II.

TABLE II

Comp. No.	Antibacterial test. M.E.D.		Fungicidal test. (Dilution below which spore gernation does not take place).
	E. Coli.	Staph. aureus.	
1	1 : 1,000	1 : 1,000	1 : 18,000
2	1 : 1,000	1 : 1,000	1 : 15,000
3	1 : 1,000	1 : 1,000	1 : 15,000
4	1 : 1,000	1 : 1,000	1 : 20,000
5	1 : 1,000	1 : 1,000	1 : 18,000
6	1 : 1,000	1 : 1,000	1 : 18,000
7	1 : 1,000	1 : 1,000	1 : 12,000
8	1 : 1,000	1 : 1,000	1 : 12,000
9	1 : 1,000	1 : 1,000	1 : 15,000
10	1 : 1,000	1 : 1,000	1 : 15,000
11	1 : 2,000	1 : 2,000	1 : 30,000
12	1 : 2,000	1 : 2,000	1 : 25,000
13	1 :50,000	1 :25,000	1 : 75,000
14	1 :75,000	1 :50,000	1 :100,000
15	1 :75,000	1 :50,000	1 :100 000
16	1 :50,000	1 :30,000	1 : 75,000
17	1 :50,000	1 :30,000	1 :100,000
18	1 :75,000	1 :50,000	1 :100,000
19	1 :25,000	1 :10,000	1 : 75,000
20	1 :25,000	1 :10,000	1 :100,000
21	1 :25,000	1 :10,000	1 : 75,000
22	1 :25,000	1 :10,000	1 : 75,000
23	1 :75,000	1 :40,000	1 :150,000
24	1 :60,000	1 :50,000	1 :150,000

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STEROID SAPOGENINS FROM INDIAN DIOSCOREA PLANTS. PART II

By A. K. Barua, * (Mrs) D. Chakravarti and R. N. Chakravarti

Eleven different species of Indian Dioscorea plants, other than those already described in Part I, have been examined for the presence of saponin. It has been possible to isolate diosgenin in 3.35% yield from the yams of *Dioscorea deltoidea* by hydrolysis of the saponin. *D. deltoidea* is thus one of the richest source for this valuable steroid sapogenin.

In view of the importance of diosgenin as a valuable starting material for the preparation of steroid hormones including cortisone, it became desirable to carry out a chemical investigation of the yams of Indian Dioscorea plants. An account of the results obtained in the case of the yams of *D. alata*, *D. glabra*, *D. esculenta*, *D. oppositifolia*, *D. wallichii*, *D. pubera*, *D. prazeri* and *D. pentaphylla* was reported in Part I (this *Journal*, 1954, **31**, 173). Of the eight specimens of yams investigated, *D. esculenta* and *D. prazeri* yielded 0.17% and 2.1% of diosgenin respectively.

In the present communication an account of the results obtained in the case of eleven other yams of the Dioscorea family is being reported. These are *D. tomentosa*, *D. bulbifera*, *D. sativa*, *D. hispida*, *D. nummularia*, *D. bellophylla*, *D. aculeata*, *D. deltoidea* and unidentified species No. 1, 2 and 3. Examination of each individual specimen of yams was carried out following the same procedure as stated in Part I (*loc. cit.*).

D. tomentosa Koen, ex.Roxb. is a climber, twining to the left. The tubers grow in bunches, each one almost cylindrical throughout and about 10 cm. in length and 4 cm. in diameter with soft white edible flesh. Fresh yams contain about 72% of moisture. In the fractional solvent extraction, only the alcoholic fraction was found to contain traces of saponin.

D. bulbifera Linn. is a climber, twining to the left. Usually one yam grows per plant. It is globose in shape and has a purplish black skin, covered with a large number of feeding roots. Bulbils are abundant. When fresh, it contains about 68% of moisture. In the fractional solvent extraction, only the alcoholic fraction showed the presence of saponin in small amounts.

D. sativa Linn. is a climber, twining to the left. In this case, only the alcoholic fraction showed the presence of traces of saponin.

D. hispida Dennst. is a climber, twining to the left. The tubers are more or less depressed globose, often lobed, sparsely coated with small roots and are extremely poisonous. Occasionally, these are of considerable size, 30-35 kg. or larger still. Due

to its poisonous nature it is known in western India as *maraposhpoli* or deadly strangle cake. The Bhils poison tigers by placing pounded tubers in the carcasses of 'kills'. A piece of the size of an apple of this tuber is sufficient to kill a man within six hours. There is intense irritation of the mouth and throat, followed by a sense of suffocation and drowsiness and finally exhaustion. These are often taken by Santhals, Kols, Bhils and Paharias after removing the poisonous alkaloid by repeated washing with hot water.

Fresh yams contain about 55% of moisture. In the fractional solvent extraction, the alcoholic fraction contained traces of saponin, and the petroleum ether, ether and, particularly, chloroform fraction showed presence of sufficient amounts of alkaloid. The poisonous character of this yam is attributed to the alkaloid, dioscorine (Boorsma, "Meded. uitis. Lands. Plant, 1894, 13 ; Schutte, *Chem. Zentrl.*, 1897, II, 130 ; Pinder and Robinson, *J. Chem. Soc.*, 1952, 2236).

D. nummularia Lam. is a climber, twining to the right. Fresh yams contain about 65% of moisture. Only the alcoholic fraction was found to contain traces of saponin.

D. aculeata Linn. is a climber, twining to the right. Usually one tuber grows per plant. The flesh is edible. The skin is often pink in colour. Fresh yams contain about 69% of moisture. None of the fractions contains any saponin.

D. deltoidea Wall. is a climber, twining to the left. The rhizomes are hard wood-like containing very little moisture and shaped like ginger. The skin is light yellow to chestnut-brown. Like *D. prazeri*, it is used by the Paharias (*i*) as an insecticide for removing lice from hair, (*ii*) as a soap for washing wool and silk and (*iii*) as a fish poison. In small doses it is used as a diuretic. The following are some of the Indian names, *kins, kildri, kithi, krithi, krits, krish* etc.

The rhizomes appear to contain 20% moisture. Both the ethy acetate and alcoholic fractions were found to contain saponin, the proportion in the latter fraction being considerable. On working up in the usual way, as described in Part I, it gave 3.35% diosgenin, m.p. 204-206° ; acetate, m.p. 194-95° and benzoate, m.p. 236-37°.

Unidentified Species

No. 1. It appeared to contain about 78% moisture. None of the fractions was found to contain any saponin.

No. 2. It was found to contain about 60% moisture. None of the fractions was found to contain any saponin.

No. 3. The yams were found to contain about 59% moisture. The alcoholic fraction was found to contain saponin in small amounts. Detailed work has not been possible for the paucity of the material.

Out of the nineteen different Indian yams investigated, *D. prazeri* of Darjeeling containing 2.1% and *D. deltoidea* of Kashmir, 3.35% diosgenin, are evidently two of the richest sources of this valuable raw material (Table I).

TABLE I

Diosgenin contents of plants of Indian and Foreign origin.

Name of plant.	Yield of diosgenin per 1000 g. dry yams.	Name of plant.	Yield of diosgenin per 1000 g. of plant.
Mexican Dioscorea:		American Trillium:	
D. bulbifera ...	4.5 g.	*T. declinatum* ...	5.0
D. capillaris ...	2.2	*T. erectum* ...	3.0
D. composita ...	3.0	*T. hugeri* ...	3.0
D. cyphocarpa ...	2.0	*T. ludovicianum* ...	5.0
D. dugessi ...	2.0	*T. recurvatum* ...	4.0
D. galeottiana ...	4.0	*T. simile* ...	4.0
D. grandifolia ...	1.5	*T. vaseyi* ...	0.4
**D. hirsuticaulis* ...	1.5		
**D. hirticaulis* ...	4.4		
D. jaliscana ...	3.1		
D. lobata ...	5.0	Mexican Balanites:	
D. macrostachya ...	2.9	(per 1000 g. of pericarp of seed)	
D. mexicana ...	3.9		
D. militaris ...	3.3	*B. aegyptica* ...	5.0
D. minima ...	2.7		
D. multinervis ...	2.7		
D. platycalpata ...	3.0		
D. plumifera ...	4.1	Indian Balanites.	
D. pringlei ...	3.5	(per 1000 g. of dried yams)	
**D. quartenata* ...	4.4		
D. remotiflora ...	3.7	*B. roxburgii* ...	1.0
D. subtomentosa ...	4.4		
D. testudinaria ...	5.0		
D. ulinei ...	4.0	Indian Dioscorea.	
D. ureeolata ...	4.6		
		D. deltoidea ...	33.5
D. composita ...	12-30	*D. esculenta* ...	1.7
D. villosa ...	10-20	*D. prazeri* ...	21.0

* Undried yams used.

EXPERIMENTAL

Fractional extraction with various solvents.—Weighed amounts of the air-dried, powdered yams of different varieties of Indian Dioscorea plants were extracted with petroleum ether (b.p. 40°-60°), ether, chloroform ethyl acetate and alcohol (90%). The

solvent of each fraction was evaporated and the residual products tested for the presence of saponin. The percentages of the solvent-extracts from different solvents are shown in Table II.

TABLE II

Name of the plant.	Pet. ether.	Ether.	$CHCl_3$.	EtAc.	EtOH	Total extract.
D. tomentosa	0.44%	0.71%	0.43%	1.05%	0.52%	3.15%
D. bulbifera (Indian)	0.41	0.55	0.58	1.27	1.61	4.42
D. sativa	0.45	1.43	0.37	1.85	0.99	5.09
D. hispida (Indian)	0.41	0.67	0.95	1.18	0.94	4.15
D. nummularia	0.53	0.78	0.54	1.35	3.23	6.43
D. aculeata	0.66	0.32	0.28	0.92	0.86	3.04
D. deltoidea	1.00	1.03	1.07	3.71	21.01	27.82
Unidentified species :						
No. 1	0.71	0.98	0.24	1.15	10,30	13.38
No. 2	0.67	0.66	0.28	2.92	1.44	5.97
No. 3	0.53	0 49	0.27	1.44	8.13	10.86

D. tomentosa Koen, ex. Roxb.—Only the alcoholic fraction was found to contain traces of saponin. It was not possible to isolate the sapogenin in any appreciable amount.

D. bulbifera Linn.—A small amount of saponin was found fo be present only in the alcoholic fraction. The crude saponin fraction isolated from the yams, following the general procedure as described in Part I, on hydrolysis yielded a small amount of a solid mass which appeared to be a mixture of sapogenins. The constituents could not be separated due to the poor yield of the crude sapogenin fraction.

D. sativa Linn.—Only a small amount of the sample of the dry yams was available. In fractional solvent extraction only the alcoholic fraction showed the presence of saponin. No crystalline sapogenin could be isolated on hydrolysis of the saponin fraction.

D. hispida Dennst.—The alcoholic fraction was found to contain traces of saponin and the petroleum ether, ether and, particularly, chloroform fraction showed the presence of sufficient amounts of alkaloid. On account of the low yield isolation of the pure sapogenin was not possible.

D. nummularia Lam.—Examination of the various fractions showed the presence of traces of saponin in the alcoholic fraction. Due to low yield it was not possible to isolate the sapogenin in a pure state.

D. aculeata Linn.—No saponin was found to be present in fractional solvent extraction.

D. deltoidea Wall.—Both the ethyl acetate and the alcoholic fractions were found to contain considerable amounts of saponin, the proportion in the latter fraction being

much higher than that in the former. As regards isolation of the pure sapogenin, the method described in detail in Part I for isolation of diosgenin from *D. esculenta* and *D. prazeri* was adopted. The product obtained after crystallisation from absolute alcohol gave colorless needles of diosgenin, m. p. 204-206°, $[\alpha]_D^{30}$-128°.7 ($CHCl_3$), yield 3.35%. It was, however, observed that satisfactory yield could be obtained only when working with small amounts, say, 100 g. of the powdered rhizomes. While working with larger amounts, the extraction was not satisfactory and the yield of diosgenin often dropped down to even 1 %. It gave no depression in mixed melting point with an authentic specimen of diosgenin. (Found : C, 78.4 ; H, 10.0. Calc. for $C_{27}H_{42}O_3$: C, 78.2 ; H, 10.1 per cent).

The *acetate* was obtained in the usual way by gently refluxing the pure sapogenin (0.1 g.) with freshly distilled acetic anhydride (0.25 c.c.) for half an hour. It crystallises in colorless needles from absolute alcohol, m.p. 194-95°, $[\alpha]_D^{31}$-119°.5 ($CHCl_3$). It gave no depression in mixed melting point with an authentic specimen of diosgenin acetate. (Found : C, 76.1 ; H, 9.5. Calc. for $C_{29}H_{44}O_4$: C, 76.3 ; H, 9.6 per cent).

The *benzoate* was obtained by dissolving the pure sapogenin (0.2 g.) in 2 c.c. pyridine. The solution on cooling was treated with a few drops of benzoyl chloride and kept overnight. It was worked up in the usual way when diosgenin benzoate was obtained in colorless needles, m.p. 236-37°, $[\alpha]_D^{31}$-81°.5 ($CHCl_3$). It gave no depression in mixed melting point with an authentic specimen of diosgenin benzoate. (Found : C, 78.7 ; H, 8.8. Calc. for $C_{34}H_{46}O_4$: C, 78.7 ; H, 8.9 per cent).

Among the three unidentified species examined, only in No. 3, the alcoholic fraction was found to contain saponin in traces. As the yield was very low it was not possible to isolate the pure sapogenin.

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PRODUCTION OF 12- AND 18-HYDROXYSTEARIC ACIDS AND SOME USEFUL COMPOUNDS DERIVED FROM THEM

By A. S. Gupta and J. S. Aggarwal

12- & 18-Hydroxystearic acids have been prepared from castor and kamala seed oils respectively using commercial nickel catalysts. Both the acids have been lactonised. Experimental details for the oxidation of 18-hydroxystearic acid, using potassium dichromate and sulphuric acid, for obtaining hexadecamethylene-1:16-dicarboxylic acid are reported.

Castor and kamala seed oils are the two major sources of 12-hydroxy-and 18-hydroxystearic acids respectively. These acids have been prepared in good yields by using commercial nickel catalysts. For the preparation of 12-hydroxystearic acid a concentrate of tri-ricinolein was obtained from castor oil. The hydrogenation of this material, either as such or in presence of a solvent, using Ruffert nickel catalyst or preferably Raney nickel catalyst, and subsequent hydrolysis and purification of the hydrogenated product furnished 12-hydroxystearic acid in a sufficiently good yield.

18-Hydroxystearic acid has now been prepared by the hydrogenation of kamlolenic acid (Gupta, Sharma and Aggarwal, *J. Sci. Ind. Res.*, 1952, **11B**, 463) in alcohol solution in presence of nickel catalyst instead of platinum catalyst, used earlier (Aggarwal *et al.*, *ibid.*, 1948, **7B**, 136). Both the hydroxystearic acids have been lactonised in benzene solution using *p*-toluenesulphonic acid as a catalyst by the method of Stoll and Rouve (*Helv. Chim. Acta*, 1934, **17**, 1238) as modified by Toyama and Hirai (*Res. Rept. Nagoya Ind. Sci. Res. Inst.*, 1952, **5**, 36) for the lactonisation of 14-hydroxypalmitic acid. The yield of lactone from 18-hydroxystearic acid was about 76% of the theoretical, but with 12-hydroxystearic acid, 7.4% yield could be obtained.

Favourable conditions for the oxidation of 18-hydroxystearic acid to hexadecamethylene-1 : 16-dicarboxylic acid, by using chromic acid in acetic acid solution or preferably potassium dichromate in sulphuric acid, have also been worked out. Gupta *et al.* (*loc. cit.*) carried out the above oxidation with potassium permanganate in acetone solution.

Experimental

12-Hydroxystearic Acid from Castor Oil

Tri-ricinolein in about 74% yield was obtained from castor oil by the method of Achaya and Saletore (*Analyst*, 1952, **77**, 375). Hydrogenation in all cases was carried out in a Parr's medium pressure hydrogenation apparatus in which the temperature and pressure of hydrogenation could be controlled.

Hydrogenation without the solvent.—Tri-ricinolein (200 g.) was hydrogenated in presence of Ruffert nickel catalyst (8 g.) at 145°-155° at 220-400 lbs./sq. in. After 7 hours the iodine value came down to 5-7 which could not be reduced further. The catalyst was filtered off and the hydrogenated product was crystallised from ethyl acetate or alcohol, m.p. 85-86°; I. V. 3.8 ; acetyl value, 150.1.

Hydrogenation in presence of solvent.—Tri-ricinolein (200 g.) was taken in alcohol (600 c.c.) and hydrogenated in presence of Raney nickel catalyst (4 g.) at 300-400 lbs./sq. in. The temperature was first kept at 100°-110° and gradually raised to 150°. After hydrogenation for 3 hours, the iodine value was 2.8. The catalyst was filtered off and the solvent distilled off. The hydrogenated product had acetyl value of 155.4.

Fatty acids were liberated from the hydrogenated product by the usual saponification method, and were crystallised from alcohol or ethyl acetate, yield 85%, m. p. 81-81.5°, I. V. < 1. (Found : Acetyl value, 158.9 ; C, 71.8 ; H, 12.3. Calc. for $C_{18}H_{36}O_3$: acetyl value, 164 ; C, 71.94 ; H, 12.0 per cent).

18-Hydroxystearic Acid from Kamala Seed Oil

Kamlolenic acid (200 g.), isolated by the method of Gupta *et al.* (*loc. cit.*), was taken in alcohol (600 c.c.) and hydrogenated in presence of Raney nickel catalyst (4 g.) at 300-350 lbs./sq. in. at 90° for first three hours and then raising to 100° for a further period of 4 hours. The catalyst was filtered off and the hydrogenated acid was freed of the solvent. After crystallisation from ethyl acetate or ethyl alcohol it melted at 95-97°, I. V. 1.2, yield 90%. (Found : Acetyl value, 160.5 ; C, 71.85 ; H, 11.87. Calc. for $C_{18}H_{36}O_3$: acetyl value, 164 ; C, 71.94 ; H, 12.0 per cent).

Lactonisation of 18-Hydroxystearic Acid.—18-Hydroxystearic acid (10 g.) was lactonised in 0.15% solution in benzene, using *p*-toluenesulphonic acid as a catalyst by the method of Toyama and Hirai (*loc. cit.*). After the reaction the solution was successively washed with water, 2% sodium carbonate solution, again with water and finally dried over anhydrous sodium sulphate. Benzene was distilled off and the residue was dissolved in 200 c.c. of *n*-hexane. The insoluble residue (0.8 g.) after crystallisation from benzene melted at 113-13.5°, and was dimeric lactone, M. W. 563. (Found : C, 76.23 ; H, 11.9. $C_{36}H_{68}O_4$ requires C, 76.53 ; H, 12.13 per cent).

From the filtrate, hexane was distilled off when 8.7 g. of the crude lactone was obtained. This was fractionated and 7.64 g. of a fraction boiling at 130°-140°/0.2-0.3 mm. was obtained. Sap. value, 197.4 (calc. 198.9) ; M. W. (cryoscopic), 280.8. (Found : C, 76.84 , H, 12.14. $C_{18}H_{34}O_2$ requires C, 76.53 ; H, 12.13 per cent).

If the lactonisation is carried out in a more concentrated solution, the yield of dimeric lactone increases.

Lactonisation of 12-Hydroxystearic Acid.—12-Hydroxystearic acid (10 g.) was lactonised as above. The benzene solution was freed of the sulphonic acid by washing with water and the solvent distilled off. The residue had an acid value 114.3. It was boiled with 200 c.c. of *n*-hexane when 3.8 g. of a solid, m.p. 81-82°, was obtained. Mixed m. p. with 12-hydroxystearic acid indicated it to be the original unchanged material. The hexane solution was washed with 2% sodium carbonate solution and then dried. The solvent was removed when about 6 g. of a semisolid material was obtained. This was subjected to vacuum distillation and 0.7 g. of a liquid material boiling at 174-76°/1-2 mm. was obtained ; M. W. (cryoscopic), 283.6. (Found : C, 76.89 ; H, 12.13. $C_{18}H_{34}O_2$ requires C, 76.53 ; H, 12.13 per cent). The residue could not be crystallised from any solvent.

Hexadecamethylene-1 : 16-dicarboxylic Acid

A mixture of potassium dichromate (37.5 g.) and sulphuric acid (1 : 2, 187 c.c.) was warmed at 90°-95° and 18-hydroxystearic acid (25 g.) was added in small lots during one hour. The heating and continuous stirring were maintained for another 3 hours after which the temperature was slowly raised to 120°-125°. After heating for 4 hours, the reaction product was cooled and then diluted with a large volume of water. The separated solid (24.7 g.) was crystallised from acetone, yield 22 g., m.p. 123-24° ; mixed m. p. with an authentic specimen, 123.3-124.5°.

The dicarboxylic acid in only 50% yield could be obtained by the oxidation of 18-hydroxystearic acid with chromic acid in glacial acetic acid solution. Some chromium salt of the acid was also obtained and the crude dicarboxylic acid was purified by boiling with sulphuric acid (1 : 1) before crystallisation.

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INTERACTION OF THIONYL CHLORIDE AND AROMATIC HYDROXY KETONES AND THEIR DERIVATIVES IN PRESENCE OF FINELY DIVIDED COPPER. PART X. PREPARATION OF 3 : 3′-DI-BENZOYL-2 : 6-2′ : 6′- AND -4 : 6-4′ : 6′-TETRAHYDROXY-DIPHENYL THIOETHERS AND THEIR DERIVATIVES

By V. J. Dalvi and G. V. Jadhav

Preparation of 3 :3′-dibenzoyl-2 :6-2′ :6′-tetrahydroxydiphenyl thioether (I) and 3 :3′-dibenzoyl--4 :6-4′ :6′-tetrahydroxydiphenyl thioether (II) is described. Bromination of (I) in acetic acid medium affords 3 :3′-dibenzoyl-2 :6-2′ :5′-tetrahydroxy-5 :5′-dibromodiphenyl thioether and of (II) yields 3 :3′-dibenzoyl-4 :6-4′ :6′-tetrahydroxy-5 :5′-dibromodiphenyl thioether. Both these dibromo-thioethers furnish the same 2 :4-dihydroxy-3-bromo-5-nitrobenzophenone on treatment with nitric acid. Their tetra-acetyl, dimethyl and tetramethyl derivatives as well as 2 : 4-dinitrophenylhydrazones have been prepared.

The investigation reported in this communication is in continuation of Part VIII of this series (this *Journal*, 1956, **33**, 440). 2 :4-Dihydroxybenzophenone, when treated with thionyl chloride and copper in presence of chloroform at room temperature, furnishes two thioethers—(I), soluble and (II), insoluble in chloroform. Bromination in presence of acetic acid affords different bromo-thioethers, viz., (VI) and (XIII) respectively, which yield the same 2 :4-dihydroxy-3-bromo-5-nitrobenzophenone (VIII). This points out that bromine in (VI) undergoes migration during the interaction with nitric acid. Such a migration is known in the case of the nitration of 4 :6-dibromoresorcinol-3-benzoate (Hodgson and Dyson, *J. Chem. Soc.*, 1935, 946). Similar migration of bromine has been observed by the present authors in the case of the action of nitric acid on 2.4-dihydroxy-5-bromobenzophenone, when the bromo-nitro derivative obtained is found different from the bromination product of 2 :4-dihydroxy-3-nitrobenzophenone, but identical with the bromination product of 2 :4-dihydroxy-5-nitrobenzophenone (under publication in the Journal of the University of Bombay).

Bromination with an excess of bromine solution and heating for some time on a boiling water-bath furnished 2 :4-dihydroxy-3 :5-dibromobenzophenone in the case of both the thioethers. These experiments throw no light on the constitution of the thioethers.

The thioether obtained from 2 :4-dihydroxy-5-bromobenzophenone by the action of sulphur dichloride is found to be identical with the dibromo derivative of (I), and hence, it is assigned the constitution 3 : 3′-dibenzoyl-2 : 6-2′ : 6′-tetrahydroxydiphenyl thioether.

There are two possible positions where the two nuclei can be linked through the sulphur atom. These are *meta* to the ketonic group and *ortho* to both the hydroxy groups or *ortho* to one hydroxy group and *para* to the other, *i. e.* 3 or 5 respectively. The thioether (II) should therefore be 3 : 3′-dibenzoyl-4 : 6-4′ : 6′-tetrahydroxydiphenyl thioether.

Further, it is found that from 2-hydroxy-4-methoxybenzophenone, only one thioether is obtained by the action of thionyl chloride and copper, and this is found to be identical with 3 : 3′-dibenzoyl-4 : 4′-dihydroxy-6 : 6′-dimethoxydiphenyl thioether obtained by methylation of (II).

That the mechanism of the thioether formation from thionyl chloride and copper is due to the intermediate formation of sulphur monochloride and sulphur dichloride *in situ*, as reported by Hirwe, Jadhav and Chakradeo (*J. Amer. Chem. Soc.*, 1935, **57**, 101), is supported in the present work by the fact that the thioether (I) is formed by the interaction of 2 : 4-dihydroxybenzophenone and sulphur monochloride, whereas the thioether (II) is formed when it is allowed to react with sulphur dichloride.

EXPERIMENTAL

3 : 3′-Dibenzoyl-2 : 6-2′ : 6′-tetrahydroxydiphenyl Thioether (I).—Thionyl chloride (9 c. c.) was gradually added (over half an hour) to the cooled suspension of 2 : 4-dihydroxybenzophenone (13 g.) and copper powder (6 g.) in dry chloroform (100 c.c.). The reaction mixture was left for 36 hours at room temperature and then filtered and the residue washed several times with dry chloroform. A yellow sticky solid was left behind after removal of chloroform (room temperature). It was first washed with petroleum ether (b.p. 40°-60°) and then treated with benzene to remove stickiness. The solid, thus formed, was treated with a little alcohol and then crystallised from acetic acid in tiny, pale yellow needles, m. p. 246-47°, yield 1 g. (Found : S, 7.0. $C_{26}H_{18}O_6S$ requires S, 6.99 per cent).

It develops a purple coloration with alcoholic ferric chloride solution. This thioether (I) was also obtained when dry ethereal solution of 2 : 4-dihydroxybenzophenone (2g. in 40 c. c.), cooled in ice, was treated with sulphur monochloride (2 c. c.) and the reaction was allowed to proceed for 1 hour at that temperature. The paste remaining after removal of the ether (room temperature) was boiled with water, when it solidified. It was extracted with alcohol and the solid obtained from alcohol on evaporation was crystallised from acetic acid in pale yellow needles, m. p. 246-47°, yield 1 g.

3 : 3′-Dibenzoyl-4 : 6-4′ : 6′-tetrahydroxydiphenyl Thioether (II).—The chloroform-insoluble portion in the above experiment was repeatedly boiled with HCl (dil.) to remove cuprous chloride. The residue was finally crystallised from acetic acid in yellow needles, m. p. 236-37°, yield 5 g. (Found : C, 67.8 ; H, 4.0 ; S, 7.3. $C_{26}H_{18}O_6S$ requires C, 68.1; H, 3.9; S, 6.99 per cent).

This is more soluble in alcohol and acetic acid than the thioether (I). It also develops a purple coloration with alcoholic ferric chloride.

The thioether (II) was also formed when sulphur dichloride (1 c.c.) was added to the well-cooled solution of 2 : 4-dihydroxybenzophenone (2 g.) in dry ether (40 c. c.). The reaction mixture was kept for 1 hour at room temperature. A yellow paste remained behind when ether was removed (room temperature). It afforded a solid

when treated with petroleum ether (40°-60°). It was then treated with benzene and finally crystallised from acetic acid in yellow needles, m. p. 236-37°, yield 0.5 g.

The *tetra-acetyl derivative* (III) of the thioether (I) was obtained by its acetylation with acetic anhydride in presence of a few drops of pyridine and heating the mixture on a boiling water-bath for half an hour. It crystallised from dilute alcohol in colorless needles, m. p. 121-22°. (Found: S, 5.4. $C_{34}H_{26}O_{10}S$ requires S, 5.1 per cent).

6:6'-*Dimethyl derivative* (IV) of the thioether (I) was formed when 0.5g. of it was heated on a boiling water-bath for 10 hours with dimethyl sulphate (0.25 c. c.) and anhydrous potassium carbonate (1 g.) in presence of dry acetone. The solid obtained from acetone solution was crystallised from alcohol (charcoal) in shining needles, m.p. 181-82°. (Found: C, 68.8 ; H, 4.3 ; S, 6.4. $C_{28}H_{22}O_6S$ requires C, 69.13 ; H, 4.52 ; S, 6.58 per cent).

Tetramethyl derivative (V) of the thioether (I) was formed when the thioether (I) was heated with more dimethyl sulphate. The solid obtained from acetone solution was first heated with 5% NaOH solution and then crystallised from alcohol in colorless needles, m. p. 159-60°. (Found: C, 69.8 ; H, 4.9 ;. S, 6.5. $C_{30}H_{26}O_6S$ requires C, 70.03 ; H, 5.06 ; S, 6.2 per cent).

2:4-*Dinitrophenylhydrazone* of (I) was obtained in dark red needles from acetic acid, m. p. 210-11° (decomp.). (Found: N, 14.1. $C_{38}H_{28}O_{12}N_8S$ requires N, 13.7 per cent).

5:5'-*Dibromo derivative* (VI) of (I) was obtained when (I: 0.9 g.) was suspended in hot acetic acid (10 c. c.) and bromine solution in acetic acid (3.2 c. c. of 20%, w/v) was gradually added to it. A white product separated which was crystallised from acetic acid in colorless needles, m.p. 220-21°. (Found: Br, 25.8. $C_{26}H_{16}O_6Br_2S$ requires Br, 25.97 per cent).

2:4-*Dihydroxy-5-bromobenzophenone* was obtained when a solution of bromine in acetic acid (15 c. c. of 20%, w/v) was added to the suspension of 2:4-dihydroxybenzophenone (4.3 g.) in acetic acid (5 c. c.) and the reaction mixture left overnight at room temperature and then diluted. The solid obtained was crystallised from dilute alcohol in colorless needles, m. p. 148-49°. (Found: Br, 27.5. $C_{13}H_9O_3Br$ requires Br, 27.3 per cent).

The same thioether (VI) was also obtained from 2:4-dihydroxy-5-bromobenzophenone when sulphur dichloride (1 c. c.) was added to its ice-cooled solution in dry ether (1g. in 20 c. c.) and the mixture was left at room temperature for 1 hour. When the ether was removed (room temperature), a semi-solid was obtained which was first washed with low-boiling petroleum ether and then extracted with alcohol. The solid obtained on removal of alcohol was crystallised from acetic acid, m. p. 220-21°. No depression was observed when mixed m. p. with (VI) was taken.

2:4-*Dihydroxy*-3:5-*dibromobenzophenone* (VII).—The thioether (I: 0.5g.), suspended in acetic acid (5 c. c.), was mixed with bromine solution in acetic acid (1 c. c. in 25 c. c.) and heated on a boiling water-bath for 4 hours. When diluted with some

water a crystalline solid separated which was crystallised from dilute alcohol in white needles, m. p. 150-51°. (Found : Br, 42.8. $C_{13}H_8O_3Br_2$ requires Br, 43.0 per cent). It showed no lowering in m. p. with the genuine specimen prepared by treating the suspension of 2 : 4-dihydroxybenzophenone (2 g.) in acetic acid (5 c. c.) with acetic acid solution of bromine (2.5 c. c. in 25 c. c. of acid) and leaving the mixture overnight at room temperature. Crystals that had separated were filtered, washed and crystallised from dilute alcohol in white needles, m. p. 150-51°. (Found : Br, 42.8. $C_{13}H_8O_3Br_2$ requires Br, 43.0 per cent).

The thioether (II) also afforded the same dibromo derivative (VII) with bromine solution under similar conditions.

2 : 4-*Dihydroxy-3-bromo-5-nitrobenzophenone* (VIII).—Nitric acid (*d* 1.4, 5 c.c.) was gradually added to an ice-cooled suspension of the dibromo-thioether (VI : 1 g.) in acetic acid (10 c. c.). It was left at room temperature for about one hour and then poured over crushed ice. The solid obtained was crystallised from acetic acid in yellow plates, m. p. 208-209°. (Found : Br, 23.5. $C_{13}H_8O_5NBr$ requires Br, 23.7 per cent). It showed no lowering in m. p. with the genuine specimen prepared (*vide infra*).

The same thioether (VIII) was formed by the action of nitric acid on the thioether (XIII) under identical conditions.

Tetra-acetyl derivative (IX) of the thioether (II) was obtained from thioether (II) in the same way as (III) was obtained from (I). It crystallised from dilute alcohol in shining, colorless, rhombic plates, m. p. 146-47°. (Found : S, 5.3. $C_{34}H_{26}O_{10}S$ requires S, 5.1 per cent).

6 : 6′-*Dimethyl derivative* (X) of the thioether (II) was prepared and crystallised in the same way as (IV) was obtained from (I), m.p. 182-83°. (Found : C, 68.9 ; H, 4.3; S, 6. 3. $C_{28}H_{22}O_6S$ requires C, 69.13 ; H, 4.52 ; S, 6.58 per cent). It developed a bottle-green colour with alcoholic ferric chloride.

The same thioether (X) was prepared from 2-hydroxy-4-methoxybenzophenone in the same way as thioether (I). The pasty mass obtained from chloroform solution was boiled with water, after treatment with petroleum ether (40°-60°), when it solidified. It was finally crystallised from alcohol in yellow plates, m. p. 182-83°, yield 2 g. from 4.5 g. of the ketone.

2-*Hydroxy 4-methoxybenzophenone* furnished (X) on treatment with sulphur monochloride or sulphur dichloride also under similar condition as (I) was prepared from 2 : 4-dihydroxybenzophenone ; yield 1 g. from 4 g.

The *tetramethyl derivative* (XI) of the thioether (II) was prepared in the same way as (V) was prepared from (I). It was crystallised from acetic acid in colorless cubes, m. p. 148-49°. (Found : S, 6.4. $C_{30}H_{26}O_6S$ requires S, 6.2 per cent). It showed no coloration with alcoholic ferric chloride.

2 : 4-*Dinitrophenylhydrazone* of (II) was obtained as dark red needles, m. p. 284-85° (decomp.). (Found : N, 13.8. $C_{38}H_{28}O_{12}N_8S$ requires N, 13.7 per cent).

2 : 4-*Dihydroxy*-5-*nitrobenzophenone* (XII).—Nitric acid (*d* 1.4, 5 c. c.) was gradually added to the thioether (II : 1 g.), suspended in acetic acid (10 c. c.). After 1 hour, it was diluted with ice and the yellow solid separating was crystallised from alcohol in pale yellow shining needles, m.p. 144-45°. (Found : N, 5.7. $C_{13}H_9O_5N$ requires N, 5.4 per cent). It showed no lowering in m. p. with the nitration product of 2:4-dihydroxybenzophenone, prepared as shown below.

Nitric acid (*d* 1.4, 50 c. c.) was gradually added to the ice-cooled acetic acid solution of the ketone (10 g.) in the acid (100 c.c.). The mixture was then left at room temperature until the temperature rose to 60°. It was poured over crushed ice and the solid obtained was finally crystallised from alcohol in pale yellow shining needles, m. p. 144-45°. (Found : N, 5.7. $C_{13}H_9O_5N$ requires N, 5.4 per cent). It developed a red coloration with alcoholic ferric chloride solution.

A solution of bromine in acetic acid (7 c. c. of 10%, w/v) was added to the hot solution of 2 : 4-dihydroxy-5-nitrobenzophenone (1g.) in acetic acid (10 c. c.). The reaction mixture was kept for 2 hours at room temperature. The yellow solid separating was crystallised from acetic acid in yellow plates, m. p. 208-209°. (Found : Br, 23.4. $C_{13}H_8O_5NBr$ requires Br, 23.7 per cent). It did not lower the melting point of (VIII) described above.

5 : 5′-*Dibromo derivative* (XIII) of the thioether (II) was prepared from the latter in the same way as (VI) was prepared from (I). It crystallised from acetic acid in clusters of tiny needles, m. p. 198-99°. (Found : Br, 25.7. $C_{26}H_{16}O_6Br_2S$ requires Br, 25.97 per cent).

The structures assigned to the bromo and the nitro derivatives of 2 : 4-dihydroxybenzophenone are the most probable ones.

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STUDIES IN INDIGOID DYES. PART XX

By Paresh Chandra Dutta and Dasrath Mandal

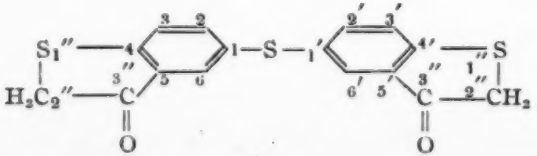
Hitherto-unknown 4:5-4′:5′-diphenyl-*bis*-(3″-hydroxy-1″-thiophene)-thioether has been prepared and condensed with *o*-diketones, and thus indigoid dyes have been prepared with the object of studying colour and chemical constitution of these dyes.

In the present communication dithioindigoid dyes have been prepared, starting from diphenyl thioether. The diphenyl thioether has been sulphonated (*Ber.*, 1893, **26**, 994) and the resulting 4:4′-disulphonic acid through acid chloride, mercaptan and dithioglycollic acid, and subsequent cyclisation has been converted into 4:5-4′:5′-diphenyl-*bis*-(3″-hydroxy″-1″-thiophene)-thioether, all unknown. This thioindoxyl has been subsequently condensed with *o*-diketones to furnish dithioindigoid dyes. The dithioindoxyl obtained in this case was very impure and could not be purified due to its susceptibility to oxidation. The yield, as compared with others reported previously, is extremely poor. It produces a violet precipitate of the *bis*-indigo when oxidised by potassium ferricyanide in alkaline solution. The dyes, excepting the isatin compound, are almost insoluble in alkaline hydrosulphite and as such a very light shade has been obtained. On a comparison of these dyes with similar dithioindigoid dyes, described in Part XVI and XVII (this *Journal*, 1955, **32**, 497 ; 1956, **33**, 54), apparently no appreciable change in colour has been noticed, but a study of the absorption spectra in xylene solution reveals that the ether linkage $-O-$ has the greatest bathochromic effect on the colour of these dyes (Table I).

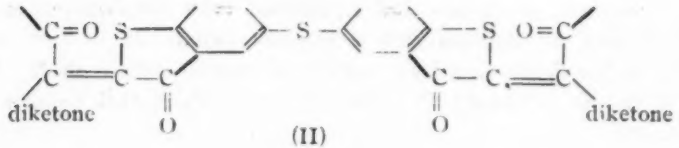
Table I

	Absorption maxima.
4:5-4′:5′-Diphenyl-*bis*-thiophenoether-2:2-*bis*-acenaphthylene-indigo	525 mμ
4:5-4′:5′-Diphenyl-*bis*-thiophenothiother-2:2-*bis*-acenaphthylene-indigo	520
4:5-4′:5′-Diphenyl-*bis*-thiophenomethane-3:3-*bis*-indol-indigo	520
4:5-4′:5′-Diphenyl-*bis*-thiophenoether-3:3-*bis*-indol-indigo	540
4:5-4′:5′-Diphenyl-*bis*-thiophenothioether-3:3-*bis*-indol-indigo	510
4:5-4′:5′-Diphenyl-*bis*-thiophenomethane-1:1-*bis*-aceanthrene-indigo	515
4:5-4′:5′-Diphenyl-*bis*-thiophenoether-1:1-*bis*-aceanthrene-indigo	520
4:5-4′:5′-Diphenyl-*bis*-thiopnenothioether-1:1- do	520

The structures of the compounds described in this paper may be represented by the following formulae :



(I)



(II)

EXPERIMENTAL

Diphenyl thioether-4:4′-disulphochloride was prepared by heating a mixture of diphenyl thioether potassium disulphonate (18 g.), PCl_5 (15 g.) and $POCl_3$ (5 c.c.) on a water-bath for 2 hours and distilling off the $POCl_3$ under reduced pressure. The resulting solid was then treated with crushed ice, filtered, washed, dried and crystallised from toluene, m.p. 157°, yield, 10.5 g. (Found: C, 37.45; H, 2.15. $C_{12}H_8O_4Cl_2S_3$ requires C, 37.6; H, 2.09 per cent).

Diphenyl thioether-4:4′-dimercaptan was prepared by heating the above disulphochloride (10 g.) with tin and HCl (conc.) for 6 hours when crystals of the mercaptan began to deposit in the inner tube of the condenser. After cooling, the solid was filtered, washed and extracted with benzene; the benzene extract was dried with $CaCl_2$, filtered and benzene distilled off. The residue was then crystallised from alcohol, m.p. 118°, yield 5 g. (Found: C, 57.51; H, 4.18. $C_{12}H_{10}S_3$ requires C, 57.6; H, 4.0 per cent).

Diphenyl thioether-4:4′-dithioglycollic acid was prepared by dissolving the mercaptan (20 g.) in 10% NaOH and warming the filtrate with monochloroacetic acid (16 g.), previously neutralised with caustic soda for an hour. The filtered solution on acidifying with HCl produced the thioglycollic acid as a white precipitate, which on crystallisation from alcohol furnished white needles, m.p. 188-89°, yield 25 g. (Found: C, 52.51; H, 4.05. $C_{16}H_{14}O_4S_3$ requires C, 52.46; H, 3.82 per cent).

4:5-4′:5′-bis-(3″-*hydroxy-1″-thiophene*)-*thioether* (I).—It was prepared by cyclising the dithioglycollic acid through its acid chloride (m.p. 77°) by anhydrous $AlCl_3$ in petroleum ether solution (b.p. 60°-80°), as described in previous communications (*loc. cit.*). This thioindoxyl, yield of which was extremely poor, could not be obtained in a pure condition. The *bis*-indigo was produced as a violet precipitate from its alkaline solution with potassium ferricyanide.

4:5-4′:5′-*Diphenyl*-bis-*thiopheno-thioether*-3:3-bis-*indol-indigo* (IIa) was prepared by mixing the separate acetic acid solutions of the dithioindoxyl and isatin and heating the mixture with HCl (conc., 1 c.c.) for half an hour when colour of the solution changed to deep red, and a violet precipitate separated out. This was filtered, washed with acetic acid and crystallised from nitrobenzene as a reddish violet crystalline mass, m.p. above 300°. It dissolves in H_2SO_4 (conc.) with a chocolate colour and dyes cotton from yellow hydrosulphite vat in pinkish violet shade. Its absorption maxima is 510 mμ. (Found: C, 65.13; H, 2.93. $C_{32}H_{16}O_4N_2S_2$ requires C, 65.30; H, 2.72 per cent).

4:5-4′:5′-*Diphenyl*-bis-*thiopheno-thioether*-2:2-bis-*acenaphthylene-indigo* (IIb) was prepared just like the previous compound from thioindoxyl and acenaphthenequi-

none as a violet-red precipitate and crystallised from nitrobenzene, m.p. above 295°. In H_2SO_4 (conc.) it dissolves with a greenish colour. It is very slightly soluble in alkaline hydrosulphite and dyes cotton in pinkish violet shade. Its absorption maxima is 520 mμ. (Found: C, 72.61; H, 2.92. $C_{40}H_{18}O_4S_2$ requires C, 72.94; H, 2.73 per cent).

4:5-4′:5′-*Diphenyl*-bis-*thiopheno-thioether*-9:9-bis-*phenanthrene-indigo* (IIc) was prepared from thioindoxyl and phenanthrenequinone as a chocolate precipitate. As the quantity was very very small it could not be properly purified and studied.

4:5-4′:5′-*Diphenyl*-bis-*thiopheno-thioether*-1:1-bis-*aceanthrene-indigo* (IId) was prepared from the thioindoxyl and aceanthraquinone as a deep chocolate precipitate and crystallised from xylene as a brownish violet mass, m.p. 278° with previous shrinking at 180°. It dissolves in H_2SO_4 (conc.) with a green colour and is almost insoluble in hydrosulphite vat, dyeing cotton in light pinkish shade. Its absorption maxima is 520 mμ. (Found: C, 75.63; H, 3.1. $C_{48}H_{22}O_4S_2$ requires C, 75.98; H, 2.9 per cent).

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THE INVERTASE ACTIVITY OF YEAST IN PRESENCE OF ACIDS AND SALTS

By M. M. Biswas

Invertase activity of brewer's yeast has been found to maintain a practically constant level in presence of constituent ions of different acids at the optimum p_H (4.5). Activity of yeast invertase, purified by dialysis and precipitation with alcohol at the optimum p_H, is appreciably influenced by different salts at the same p_H (4.5).

Influence of hydrogen-ion concentration on the activity of invertase has been thoroughly studied by different investigators. Euler and Laurin (*Z. physiol. Chem.*, 1919, **108**, 63) found yeast saccharase most stable near its optimum p_H (4.5). The method of purification of enzymes, originally developed by Willstätter and his co-workers is based on the elution of adsorbed enzymes on suitable adsorbents by changing the hydrogen-ion concentration (vide Kraut, "Methoden der Adsorption und Elution", 1928). Experiments on adsorption of enzymes by suitable adsorbents have revealed in most cases the influence of ions on the binding capacity of the adsorbents. Adsorbed enzymes, again, may be easily liberated in the free state under the influence of a suitable ionic environment. Thus, invertase was easily removed from its adsorbent alumina with a trivalent anion such as a phosphate or an arsenate. No systematic adsorption experiments, however, have been carried out to study the influence of ions on the enzymes and their activity inspite of the recent practice of isolating invertase in the chemically pure state by the use of suitable adsorbents. Adams and Hudson (*J. Amer. Chem. Soc.*, 1943, **65**, 1359) have been able to prepare invertase in a highly pure active state from yeast with bentonite as the adsorbent. As adsorption experiments are greatly influenced by the presence of ions, a systematic work on these lines appears to be necessary. The object of the present paper is to study the influence of different ions on the enzyme activity of yeast invertase, purified under different conditions.

Experimental

Dried brewer's yeast powder (100 g.) was mixed with water (150 c.c.) to form a paste. The paste was treated with toluol (20 c.c.) and stirred at 30° with a rod for about ½ hour to a thin sludge. The yeast was autolysed at this stage and the autolysed mixture was diluted with water (200 c.c.) at 30° and kept for 1 hour. Toluol (4 c.c.) was again added and the mixture was filtered with Kieselguhr under suction. The filtrate was used for each experiment (14 c.c. of the filtrate ≡ 10 g. of dried yeast powder). The substrate was 80 g. sucrose in 200 c.c. water. In the first case (Table Ia) $N/10$ solutions of hydrochloric, sulphuric, citric, oxalic and acetic acids were used to adjust p_H of the enzyme-substrate mixture to 4.5 (optimum value). Invertase activity was tested with Benedict's quantitative reagent. An aliquot portion of the digestion mixture was titrated with standard Benedict's reagent and the total amount of glucose formed by the invertase

of 10 g. yeast powder was calculated. In the second place (Table IIA), experiments were made with $N/10$ solutions of potassium chloride, sodium chloride, sodium sulphate, potassium sulphate, calcium chloride, barium chloride, aluminium chloride and potassium ferrocyanide on adjustment of p_H of the enzyme-substrate mixture to 4.5 with $N/10$ solution of acetic acid.

A parallel series of experiments was conducted with yeast invertase, purified by precipitation of the dialysed extract from crude yeast with 50% alcohol, at p_H 4.5. The activity of this enzyme was found to be of a higher order than that observed before hand. The results have been incorporated in Tables IB and IIB. Glass electrodes were used for determination of H-ion concentration or activity with a Leeds Northrup p_H-meter.

Tables IA and IIA refer to invertase extract of 10 g. yeast with substrate of 80 g. saccharose in 200 c.c. water + 2 c.c. toluol and $N/10$ acids. Tables IB and IIB refer to alcohol-purified invertase solution (29 c.c. ≡ 10 g. yeast) with substrate of 80 g. of saccharose in 200 c.c. water + $N/10$ acids at p_H 4.5.

TABLE I

Acid solution used to adjust p_H to 4.5.	A. Invertase activity (g. glucose formed by 10 g. of yeast extract).	B. Invertase activity of extract corresponding to 10 g. yeast.
HCl	0.406	4.08
H_2SO_4	0.403	4.4
Citric acid	0.406	2.5
Oxalic acid	0.403	2.3
Acetic acid	0.403	2.3

TABLE II

Vol. of $N/10$ soln. used = 10 c.c.

Electrolytes.	A. Invertase activity (g. glucose formed by 10 g. yeast extract).	B. Invertase activity of extract corresponding to 10 g. yeast.
KCl	0.385	3.4
NaCl	0.385	3.2
Na_2SO_4	0.379	2.2
K_2SO_4	0.379	3.3
$CaCl_2$	0.391	2.6
$BaCl_2$	0.391	2.2
$AlCl_3$	0.419	3.9
$K_4Fe(CN)_6$	0.419	3.1

DISCUSSION

Table I (A and B) demonstrates the influence of ions on the invertase activity of yeast. In the first place it is evident that p_H is the principal determining factor in influencing the invertase activity; the anions having little effect so far as the invertase extract, not treated with alcohol, is concerned. But in the case of the alcohol extract (vide Table IB), the activity appears to depend on the nature of the anions. Usually the organic anions depress the activity markedly.

Table II represents results on the study of the influence of the electrolytes, the p_H being adjusted to 4.5 with $N/10$ acetic acid. From Table IIA it appears that provided the p_H remains constant, the invertase activity is not seriously affected by salts in cases where no alcohol is used. But Table IIB shows greater variations, $AlCl_3$ having the highest activity while $BaCl_2$ has the least value. Whether this change in activity is to be attributed to adsorption of ions is a matter requiring a thorough study.

As observed by Adams and Hudson (*loc. cit.*), their invertase preparations consisted chiefly of protein although they still contained only a small amount of carbohydrate. Accordingly, the invertase activity of the enzyme-substrate mixture will generally be controlled by biologically active proteins of which the enzymes are composed. The author (*Ind. J. Med. Res.*, 1936, **24**, 363) observed specific adsorption of H^+ ions from oxalic acid by diphtheria antibody globulin. It has also been proved by the author (*ibid.*, 1938, **26**, 469) that normal globulin possesses a stronger affinity for H^+ ions than the antibody globulin. Ordinary proteins of the system become sensitized on immunisation and accordingly their ionic adsorption properties also change.

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INTERACTION OF AROMATIC HYDROXY KETONES AND THIONYL CHLORIDE IN PRESENCE OF FINELY DIVIDED COPPER. PART XI. PREPARATION OF 2:2′-DIHYDROXY-3:3′ - DIACETYL - AND -3:3′-DIPROPIONYL-5:5′-DIMETHYLDIPHENYL SULPHIDES AND 2:2′-DIHYDROXY-3:3′-DIMETHYL-5:5′-DIACETYLDIPHENYL SULPHIDE

By V. G. Kulkarni and G. V. Jadhav

Preparation of 2:2′-dihydroxy.3:3′-diacetyl-5:5′-dimethyldiphenyl sulphide (I), 2:2′-dihydroxy-3:3′-dipropionyl-5:5′-dimethyldiphenyl sulphide (II) and 2:2′-dihydroxy-3:3′-dimethyl-5:5′-diacetyldiphenyl sulphide (III) is described. The constitution of these sulphides has been arrived at by their interaction with nitric acid and identifying the products obtained. Their acetyl and 2:4-dinitrophenylhydrazone derivative have been prepared.

Present work is the continuation of the work published previously (this *Journal*, 1956, **33**, 266, 519). The sulphides (I), (II) and (III) are obtained wehn 2-hydroxy-5-methylacetophenone (2-acetyl-*p*-cresol, OH=1) 2-hydroxy-5-methyl-propiophenone (2-propionyl-*p*-cresol) and 3-methyl-4-hydroxyacetophenone (4-acetyl-*o*-cresol) respectively are treated with thionyl chloride in presence of finely divided copper or with sulphur monochloride or sulphur dichloride.

Action of nitric acid on (I) affords 2-nitro-6-acetyl-*p*-cresol (2-hydroxy-3-nitro-5-methylacetophenone) as proved by mixed melting point with the nitration product of 2-hydroxy-5-methylacetophenone. It is therefore assigned the constitution 2:2′-dihydroxy-3:3′-diacetyl-5:5′-dimethyldiphenyl sulphide.

Sulphide (II), however, furnishes 2:6-dinitro-*p*-cresol (-OH=1) by the action of nitric acid in presence of sulphuric acid. Nitro group in position-6 has come in place of the propionyl group and the other nitro group must have come in place of the sulphur atom joining the two nuclei. It is therefore assigned the constitution 2:2′-dihydroxy-3:3′-dipropionyl-5:5′-dimethyldiphenyl sulphide.

Sulphide (III) furnishes 4:6-dinitro-*o*-cresol (-OH=1) by the action of nitric acid in presence of sulphuric acid. Nitro group in position-4 has come in place of the acetyl group and the other nitro group must have come in place of the sulphur atom linking the two nuclei. It is therefore designated as 2:2′-dihydroxy-3:3′-dimethyl-5:5′-diacetyldiphenyl sulphide. Diacetyl and 2:4-dinitrophenylhydrazone derivatives of these disulphides have been prepared.

Experimental

2:2′-Dihydroxy-3:3′-diacetyl-5:5′-dimethyldiphenyl Sulphide (I).—Copper powder (2 g.) was slowly added (over 2 hours) to the mixture of 2-hydroxy-5-methylacetophenone (2 g.) and thionyl chloride (3 c.c.) (E. Merck) and the reaction mixture was left overnight at room temperature. It was then diluted with dry benzene and

filtered. The paste, obtained after removal of the liquid, was subjected to the action of steam for about half an hour, when it solidified to a yellowish powder. It crystallised from benzene, m.p. 100° (decomp.), yield 0.5 g.

It is soluble in benzene, acetone and carbon disulphide and insoluble in alcohol, chloroform, ether and acetic acid. (Found : C, 65.26 ; H, 5.69 ; S, 10.14. $C_{16}H_{18}O_4S$ requires C, 65.46 ; H, 5.45 ; S, 9.69 per cent).

The same sulphide was also obtained when 2-hydroxy-5-methylacetophenone (2 g.) was treated with sulphur monochloride or sulphur dichloride (2 c.c.) and allowed the reaction to proceed overnight at room temperature. Next day it was washed with dry ether to remove sulphur chloride and the paste remaining behind was subjected to the action of steam for about half an hour, when it solidified. It was crystallised from benzene, m.p. 100° (decomp.), yield 1 g. It showed no lowering in melting point with the above sulphide.

The *diacetyl derivative* of (I) was prepared by boiling it for 2 hours with acetic anhydride and pyridine. It crystallised from alcohol, m.p. 77-78°. (Found : S, 7.8. $C_{22}H_{22}O_6S$ requires S, 7.7 per cent).

The 2 : 4-*dinitrophenylhydrazone* of (I) crystallised from acetic acid, m.p. 175-76°. (Found : S, 4.7. $C_{30}H_{26}O_{10}N_8S$ requires S, 4.60 per cent).

2-*Hydroxy*-3-*nitro*-5-*methylacetophenone* (2-*nitro*-6-*acetyl*-p-*cresol*).—The sulphide (I : 1 g.) was added to HNO_3 (conc., 20 c.c.) and the mixture was warmed on a boiling water-bath for about 1 hour, when a yellowish substance separated. The mixture was then diluted with water and the product obtained was crystallised from alcohol, m.p. 130-31°. It contained nitrogen but no sulphur. It showed no depression in m.p. when mixed with an authentic specimen of 2-nitro-6-acetyl-*p*-cresol, prepared according to Bredereck *et al.* (*Ber.*, 1939, **72B**, 1414).

2 : 2′-*Dihydroxy*-3 : 3′-*dipropionyl*-5 : 5′-*dimethyldiphenyl Sulphide* (II).—Copper powder (2 g.) was gradually added to the mixture of 2-hydroxy-5-methylpropiophenone (3 c.c.) and thionyl chloride (Pure, Merck, 5 c.c.) and the mixture was refluxed on a boiling water-bath for about 3 hours. The mixture was then extracted with chloroform. The brownish paste left after removal of the solvent turned into a yellow solid on treatment with alcohol. It crystallised from benzene, m.p. 110°, yield 2 g. (Found : C, 67.01 ; H, 6.16 ; S, 9.07. $C_{20}H_{22}O_4S$ requires C, 67.03 ; H, 6.14 ; S, 8.94 per cent).

It is insoluble in alcohol and acetic acid, fairly soluble in acetone, ether and benzene, and easily in chloroform and carbon disulphide.

The same sulphide was obtained by heating the mixture of 2-hydroxy-5-methylpropiophenone (3 c.c.), sulphur monochloride or dichloride (2 c.c.) and copper powder (0.5 g.) on a boiling water-bath for 3 hours. The mixture was then extracted with dry chloroform. The reddish paste remaining behind after removal of chloroform was repeatedly washed with alcohol and then boiled with acetic acid and finally washed with water and left in water for some time, when it solidified. It crystallised from benzene, m.p. 110°, yield 0.5 g.

It showed no depression in m.p. when mixed with the above sulphide.

Diacetyl derivative of (II) was prepared by heating it with acetic anhydride in presence of pyridine and crystallised from benzene, m.p. 101-102°. (Found : S, 7.01. $C_{24}H_{26}O_6S$ requires S, 7.24 per cent).

The 2 : 4-*dinitrophenylhydrazone* of (II) crystallised from chloroform, m.p. 200-201°. (Found : S, 4.87. $C_{32}H_{30}O_{10}N_8S$ requires S, 4.56 per cent).

2 : 6-*Dinitro*-p-*cresol*.—The sulphide (II : 1 g.) was suspended in H_2SO_4 (conc., 20 c.c.) and HNO_3 (conc., 15 c.c.) was added to it, when the substance went into a yellow solution, giving out the smell of propionic acid. It was left overnight at room temperature and then diluted. The solution was extracted with ether, when a yellow solid was obtained. It contained nitrogen and no sulphur. It crystallised from alcohol, m.p. 80-81°. (Found : N, 13.9. Calc for $C_7H_6O_5N_2$: N, 14.14 per cent). It did not show any lowering in melting point when mixed with an authentic specimen prepared according to Friache (*Annalen*, 1884, **224**, 138).

2 : 2′-*Dihydroxy*-3 : 3′-*dimethyl*-5 : 5′-*diacetyldiphenyl Sulphide* (III).—3-Methyl-4-hydroxyacetophenone (2 g.) was mixed with thionyl chloride (3 c.c.), and copper powder (1 g.) was added in small quantities at a time (over 1 hour). The reaction mixture was left overnight at room temperature. It was then extracted with dry ether. The brown paste left after removal of ether was repeatedly boiled with water when ultimately it solidified. It crystallised from alcohol, m.p. 98-99° (decomp.), yield 0.8 g. (Found : C, 65.31; H, 5.62; S, 9.69. $C_{18}H_{18}O_4S$ requires C, 65.45; H, 5.45; S, 9.69 per cent).

The same sulphide was obtained by the action of sulphur monochloride or dichloride (3 c.c.) on 3-methyl-4-hydroxyacetophenone (2 g.) at room temperature and allowing the reaction to proceed overnight. It was worked up as in the case of the previous experiment. It showed no lowering in melting point with the sulphide (III).

The *diacetyl derivative* of (III) was perpared as in the case of (I) and crystallised from alcohol, m.p. 112°. (Found : S, 8.01. $C_{22}H_{22}O_6S$ requires S, 7.7 per cent).

The 2 : 4-*dinitrophenylhydrazone* of (III) crystallised from acetic acid, m.p. 158-59°. (Found : S, 4.57. $C_{30}H_{26}O_{10}N_8S$ requires S, 4.63 per cent).

4 : 6-*Dinitro*-o-*cresol*.—The sulphide (III : 1 g.) was suspended in H_2SO_4 (conc., 20 c.c.) and HNO_3 (conc., 15 c.c.) was added to it. The mixture was heated on a boiling water-bath for about half an hour, left overnight at room temperature, and then diluted with water. The resulting solution was extracted with ether when a yellowish solid was obtained. It was crystallised from alcohol, m.p. 86-87°. It contained nitrogen but no sulphur. (Found : N, 14.3. Calc. for $C_7H_6O_5N_2$: N, 14.4 per cent).

It showed no lowering in melting point when mixed with an authentic specimen prepared according to Rapp (*Annalen*, 1884, **224**, 175).

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STUDIES ON THE DEPENDENCE OF OPTICAL ACTIVITY ON CHEMICAL CONSTITUTION. PART XLIV. THE ROTATORY DISPERSION OF *o*-, *m*-, *p*- CHLOROPHENYLIMINO-*d*-CAMPHORS AND PHENYL-, *o*-, *m*-, *p*-CHLOROPHENYLAMINO-*d*-CAMPHORS

By Bawa Kartar Singh and (Miss) Shanti Kumari Seth

The rotatory dispersion of *o*-, *m*-, *p*-chlorophenylimino-*d*-camphors and phenyl-, *o*-, *m*-, *p*-chlorophenylamino-*d*-camphors has been determined in seven solvents and is found to obey one-term Drude's equation. It is therefore *simple*.

The effect of solvent and of position isomerism of substituent groups in benzene ring on the rotatory power of these compounds has been discussed.

The effect of conjugated double bonds on rotatory power, which is phenomenal in this series of compounds, as well as the '*characteristic*' absorption bands (λ_0) have also been discussed.

In previous investigations of these compounds (Forster and Thornley, *J. Chem. Soc.*, 1909, **95**, 942 ; Singh *et al.*, *ibid.*, 1919, **115**, 572 ; this *Journal*, 1950, **28**, 229) the rotatory power of *p*-chlorophenylimino-*d*-camphor was recorded in one solvent for one wave-length (Na_D) only, whereas that of *m*- and *o*-chlorophenylimino-*d*-camphor was recorded in two solvents for Na_D wave-length. In the case of the corresponding amino derivatives, the rotatory power of the *p*-chlorophenylamino-*d*-camphor was determined in one solvent for Na_D line only. In the present investigation we have determined the rotatory powers of *o*-, *m*-, *p*-cholorophenylimino-*d*-camphors and phenyl-, *o*-, *m*-, *p*-cholorophenylamino-*d*-camphors in seven solvents for thirteen wave-lengths in the visible region of the spectrum (λ=6708Å to λ=4358Å).

It may be recalled that Singh, Basu-Mallick and Bhaduri (this *Journal*, 1931, **8**, 95) determined the rotatory power of phenylimino-*d*-camphor for three wave-lengths, and of phenylamino-*d*-camphor for four wave-lengths in six solvents. Singh and Singh (*ibid.*, 1951, **28**, 229) later determined the rotatory dispersion of these compounds : whereas these values of rotatory dispersion agree in the case of phenylimino-*d*-camphor, they, however, do not agree for phenylamino-*d*-camphor. Our present values of rotatory dispersion of phenylamino-*d*-camphor agree with those of Singh, Basu-Mallick and Bhaduri (*loc. cit.*).

Nature of Rotatory Dispersion

These compounds exhibit 'simple' rotatory dispersion as their rotatory powers can be expressed by Drude's one-term equation,

$$[\alpha]_{\lambda}^{t^\circ} = \frac{k}{\lambda^2 - \lambda_0^2},$$

where k is the rotation constant and λ_0^2, the dispersion constant. The calculated values of rotatory dispersion (c) for different wave-lengths agree with the observed ones (o). The differences (o-c) are of the nature of casual experimental errors and have been omitted from Tables I-VII for economy of space : out of 532 observations of rotatory power, 69 exactly agree with the calculated values,

387 agree within ± 0.02° of the observed angle of rotation, 64 within 0.04° and the remaining 12 within ± 0.05°. The above mentioned cases, in which the differences between the observed and calculated values of rotatory power agree within ± 0.04° to ± 0.05° of the observed angle of rotation, are for wave-lengths in blue and blue-violet regions of the visible spectrum.

In Drude's equation, k may be taken as a measure of the *absolute* rotation of the compound for that value of the wave-length for which $\lambda = \sqrt{1+\lambda^2}$. The *absolute* rotation constant, k, is thus numerically, but not dimensionally, identical with the specific rotation, $[\alpha]$. A comparison of rotatory powers, $[\alpha]$, and rotation constants, k, at this wave-length λ (where $\lambda = \sqrt{1+\lambda_0^2}$) may be regarded as that for the corresponding conditions of wave-lengths in which the effects of dispersion are eliminated. This wave-length is in the near infra-red and is not much greater than 10,000 Å.

Position Isomerism and Rotatory Power

In the Tables A and B the sequence of specific rotatory powers, $[\alpha]^{35}_{5461}$, rotation constants, k, and the '*characteristic*' wave-lengths, λ_0, of phenyl-, *o*-, *m*-, *p*-chlorophenylimino-*d*-camphors (Table A) and phenyl-, *o*-, *m*-, *p*-chlorophenylamino-*d*-camphors (Table B) is given in the increasing order of their values.

TABLE A

Solvent.	$[\alpha]^{35}_{5461}$.	k.	λ_0.
Benzene	$o < m < p <$ un	$o < m < p <$ un	$o < m < p <$ un
Chloroform	$o < m < p <$ un	$o < m < p <$ un	$o <$ un $< m < p$
Ethyl acetate	$o < m < p$	$o < m < p$	$o < p < m$
Pyridine	$o < m < p <$ un	$o < m < p <$ un	$o <$ un $< p < m$
Acetone	$o < m < p <$ un	$o < m < p <$ un	$o <$ un $< m < p$
Ethyl alcohol	$o < m < p <$ un	$o < m < p <$ un	$o <$ un $< m < p$
Methyl alcohol	$o < m < p <$ un	$o < m < p <$ un	$o <$ un $< m < p$

TABLE B

Solvent.	$[\alpha]^{35}_{5461}$.	k.	λ_0.
Benzene	$o < p < m <$ un	$o < p < m <$ un	un $< p < o < m$
Chloroform	$o < p < m <$ un	$o < p < m <$ un	$p < o <$ un $< m$
Ethyl acetate	$p < o < m <$ un	$p < o < m <$ un	$m < o < p <$ un
Pyridine	$m < p <$ un $< o$	$m < p <$ un $< o$	$p < o <$ un $< m$
Acetone	$o < p < m <$ un	$o < p < m <$ un	$m < p <$ un $< o$
Ethyl alcohol	$o < p < m <$ un	$o < p < m <$ un	$p <$ un $< m < o$
Methyl alcohol	$o < p < m <$ un	$o < p < m <$ un	$p < m <$ un $< o$

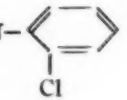
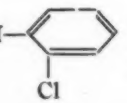
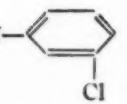
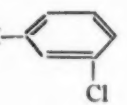
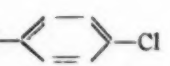
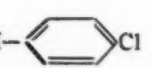
These tables show that neither Frankland's 'lever-arm hypothesis' (*J. Chem. Soc.*, 1896, **69**, 284), nor its electrostatic modification by Rule (*ibid.*, 1924, **125**, 1122), according to both of which the *meta* isomeride should be intermediate between the *ortho* and *para*, and the unsubstituted compound should be equal to, or less than the *ortho* compound as regards their rotatory effects, is followed even in a single case. On the other hand, Cohen's rule (*ibid.*, 1910, **97**, 1739) which states that the rotatory power produced by an *ortho* substituent differs more from that

of the *unsubstituted* compound, than do those of *meta* and *para* isomerides, is observed in all cases with the exception of chlorophenylamino-*d*-camphors in pyridine and ethyl acetate.

It is, however, worthy of note that the specific rotatory powers of the *ortho*-chlorophenylimino-*d*-camphor are remarkably lower than those of the *meta*, *para* and unsubstituted compounds (Table C).

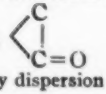
TABLE C

Specific ratatory powers, $[\alpha]^{35}_{5461}$, *in different solvents.*

Structural formula.	Benzene. [2.28]*	$CHCl_3$ [5.2]	EtAc. [6.11]	Pyridine. [12.4]	Acetone. [21.5]	EtOH [25.8]	MeOH [31.1]
1. §R = N– ‡	927.2 (123.8)	871.5 (131.6)	... ...	910.3 (139.6)	815.8 (119.3)	843.3 (128.4)	800.8 (123.4)
2. RH–NH–	155.0 (31.15)	143.0 (31.31)	124.5 (25.79)	65.5 (14.13)	121.0 (28.5)	119.0 (28.66)	115.0 (27.48)
3. R=N– 	190.0 (31.17)	188.3 (38.21)	208.5 (40.13)	305.0 (49.12)	253.2 (41.56)	203.3 (35.19)	220.0 (43.77)
4. RH–NH– 	73.5 (15.57)	109.5 (24.71)	106.5 (24.76)	75.0 (16.05)	98.0 (21.65)	87.0 (20.07)	79.0 (15.84)
5. R=N– 	656.0 (94.33)	624.0 (91.69)	596.0 (80.41)	710.0 (84.58)	574.8 (81.3)	598.3 (85.55)	553.3 (78.27)
6. RH–NH– 	126.5 (26.55)	139.0 (28.34)	123.5 (29.94)	46.5 (9.96)	107.5 (26.76)	107.0 (25.56)	103.0 (25.815)
7. R=N– 	838.0 (114.4)	865.0 (117.82)	740.0 (102.2)	852.0 (116.6)	729.9 (100.86)	758.0 (102.74)	726.6 (99.5)
8. RH–NH– 	120.0 (25.86)	118.0 (26.04)	105.0 (23.58)	54.5 (12.206)	102.0 (24.57)	98.0 (24.42)	93.0 (24.784)

* The figures in square brackets indicate dielectric constant of pure solvents.

† The values in simple brackets are the rotation constants, *k*.

§ R represents C_8H_{14} 

‡ The values of rotatory dispersion of phenylimino-*d*-camphor have been taken from Singh and Singh (this *Journal*, 1951, **28**, 229).

TABLE D

Molecular rotatory powers, $[M]^{35}_{5461}$, *in different solvents.*

*Substance.	Benzene.	Diff.	Chloroform.	Diff.	Ethyl acetate.	Diff.	Pyridine.	Diff.	Acetone.	Diff.	EtOH.	Diff.	MeOH.	Diff.
3.	523.5	319.5	518.8	214.8	573.8	278.2	840.3	642.1	697.7	425.8	560.1	318.7	606.0	386.7
4.	204.0		304.0		295.6		208.2		271.9		241.4		219.3	
5.	1807.0	1455.9	1719.0	1333.2	1642.0	1299.3	1956.0	1827.0	1583.0	1284.6	1648.0	1351.0	1524.0	1238.1
6.	351.1		385.8		342.7		129.0		298.4		297.0		285.9	
7.	2308.0	1972.2	2383.0	2052.8	2039.0	1744.8	2347.0	2195 8	2010.0	1721.4	2088.0	1816.1	2002.0	1743.9
8.	335.8		330.2		294 2		151.2		288.6		271.9		258.1	
1.	2235.0	1902.1	2100.0	1752 6	—	—	2194.0	2034.8	1966.0	1671.9	2032.0	1742.8	1930.0	1650.5
2.	332.9		347.4		302.5		159.2		294.1		289.2		279.5	

* The number of the substances corresponds to those recorded in Table C.

TABLE E

Characteristic wave-lengths (λ_o) *in* Å

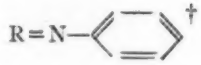
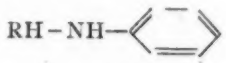
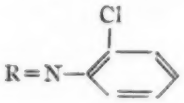
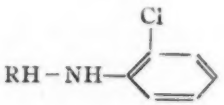
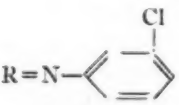
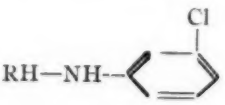
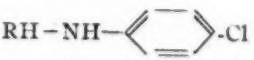
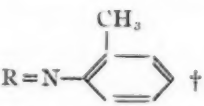
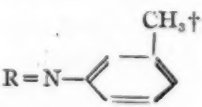
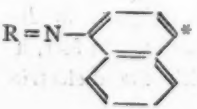
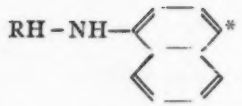
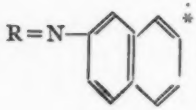
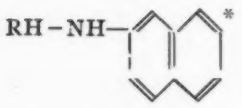
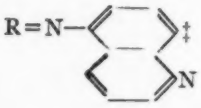
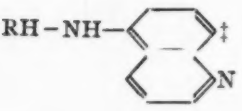
Substance.	Benzene.	$CHCl_3$	EtAc.	Pyridine.	Acetone.	EtOH.	MeOH.	Average.
	4061	3835	...	3806	3899	3821	3798	3888
	2648	2821	3028	2896	2543	2395	2348	2848, 2427
	3645	3085	3254	3697	3663	3536	3152	3635, 3164
	2963	2679	2574	2921	2775	2668	3128	2946, 2640
	3925	3889	4036	4241	3935	3911	3953	3984
	2971	3061	2392	3017	2381	2442	2159	3016, 2405, 2159
	4021	4024	4012	4017	4000	4034	4017	4018
	2893	2402	2766	2724	2449	2228	1734	2794, 2360, 1734
	3990	3802	—	3851	3842	3845	4081	3952
	3930	3987	—	3918	3886	3962	4014	3950
	4246	3954	—	4130	3869	3947	4096	4040
	3407	3304	—	3196	3274	3194	3239	3269

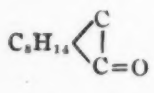
TABLE E (contd.)

	Benzene.	$CHCl_3$.	EtAc.	Pyridine.	Acetone.	EtOH.	MeOH.	Average.
	3164	3501	—	3407	3264	3268	3186	3454, 3221
	3206	3164	—	3514	3584	3472	3245	3523, 3205
	3180	3181	—	3180	3317	3214	3228	3217
	3701	3305	—	3547	3548	3347	3227	3598, 3293
	3187	3464	—	3162	3194	3164	3178	3464, 3177

† Singh and Singh, this *Journal*, 1951, **28**, 229,

* Singh and Kapur, *Proc. Ind. Acad. Sci.*, 1949, **29A**, 413.

‡ Singh and Kapur, *ibid.*, 1950, **31A**, 280.

R represents 

The sequence of rotation constants, k's, in the decreasing order of their values is the same as that of the specific rotatory powers, $[\alpha]^{35}_{5461}$. The order of the increasing value of the characteristic wave-lengths, λ_0, for the different isomerides, does not, however, run parallel to that of the other two constants, namely, $[\alpha]^{7^\circ}_{\lambda}$ and k (Tables A and B). The numerical values of these constants do not show any relationship (Tables I to III).

Influence of Solvent on Rotatory Power

Table C shows that the sequence of increase in rotatory power with decrease in dielectric constant of the solvent is in no case followed in the whole series. In fact, it would be more rational to compare the values of rotatory powers with the dielectric constants of the solutions, which are not available.

The Effect of Conjugated Unsaturation on Rotatory Power

The molecular rotatory powers, $[M]^{35}_{5461}$, of the chlorophenylimino-*d*-camphors and chlorophenylamino-*d*-camphors are shown in Table D for seven solvents. The fall in molecular rotation, $[M]^{35}_{5461}$, in passing from the arylimino-*d*-camphor to arylamino-*d*-camphor is also shown. The remarkable fall in the molecular rotatory powers of aryliminocamphors on their reduction to arylamino compounds may be correlated with a break (dotted line) in the conjugation of the double bonds of the carbonyl, azethenoid and phenyl groups present in the arylimino derivatives, thus:

$[M]^{35}_{5461} = 2313°$ (conjugation intact)

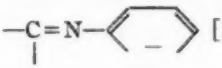
$[M]^{35}_{5461} = 336.3°$ (dotted line) (conjugation broken)

It is remarkable that the fall in rotation is most in *para*-substituted compounds and least in the *ortho*-substituted ones. The fall in the case of unsubstituted compounds is intermediate between those of *para* and *meta* derivatives.

The Influence of Solvent, Nature and Position of the Substituent Groups in the Benzene, Naphthalene and Quinoline Rings, and the Effect of Conjugated Double Bonds present in the Molecule of the Optically Active Compounds on the 'Characteristic' Wave-length (λ_0) in the Ultraviolet Region : Correlation between λ_0 and $\lambda_{(max)}$. The 'Characteristic' Ultraviolet Absorption Maximum

In Table E are recorded the '*characteristic*' wave-lengths (λ_0's), governing the rotatory power, deduced from Drude's one-term equation, in the following 17 optically active compounds, namely, phenyl-, chlorophenyl-(*o*-, *m*-, *p*-), tolyl-(*o*-, *m*-, *p*-), naphthyl-(α- and β-) and quinolinoimino-*d*-camphors and phenyl-, chlorophenyl-(*o*-, *m*-, *p*-), naphthyl-(α- and β-), and quinolinoamino-*d*-camphors.

The compounds listed in Table E fall into two groups: the arylimino- and the arylamino *d*-camphors. In the former series the conjugation between the double bonds of the carbonyl, azethenoid and the phenyl (or aryl) groups of the chromophore,



is complete.

In the case of phenyl-, chlorophenyl-(*m*-, *p*-), and tolyl- (*o*-, *m*-, *p*-)-imino-*d*-camphors, the average value of the 'characteristic' wave-length (λ_0) of the chromophore is about 3972Å, but in the case of *o*-chlorophenylimino-*d*-camphor it is considerably less, λ_0's being 3635 and 3164Å*. In the case of naphthyl-(α- and β-) and quinolinoiminocamphors, there are two 'characteristic' wave-lengths, 3558 and 3256Å. The values of λ_0 of this chromophore are, thus, lowered by the substitution of the naphthyl or quinolyl radical in place of phenyl group.

* The values of λ_0's are the average of the series in different solvents.

In the case of camphorquinone, the average value of the 'characteristic' wave-length (λ_o) in six solvents in 1% solution at 35° is 4740 Å (Singh, Basu-Mallick and Bhaduri, *loc. cit.*), whereas Lowry and Cutter report $\lambda_o = 4730$ Å in 15% benzene solution at 20° (*J. Chem. Soc.*, 1925, 607).

The chromophore of camphorquinone is also present in glyoxal, whose 'characteristic' absorption maxima (λ_{max}) are 1960 2800 and 4630 Å. Lowry and French (*ibid.*, 1924, **125**, 1921) record the 'characteristic' absorption maxima of camphorquinone as below:

Solvent.	Conc.	Log ϵ.	λ_{max}.
Alcohol	$M/250$	1.46	4650
Benzene	$M/250$	1.55	4650
,,	15 g./100 c.c.	...	4700

The value of the 'characteristic' wave-length of this compound, as mentioned above ($\lambda_o = 4740$ Å), deduced from the rotatory dispersion equation of Drude (Singh, Basu-Mullick and Bhaduri, *loc. cit.*), is, thus, practically identical with the ultraviolet absorption maximum ($\lambda_{max} = 4700$ Å). In the case of camphor, Lowry and French (*loc. cit.*) report the following values for the 'characteristic' ultraviolet absorption maxima (λ_{max}):

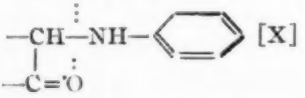
Solvent.	Conc.	Log ϵ.	λ_{max}.	*λ_o.
Alcohol	$M/100$	1.67	2880	2950, 1924
*cyclo*Hexane	$M/100$	1.45	2880	...
,,	20 g /100 c.c.	...	2900	...
Benzene	7 g /100 c.c.	1.57	2880	2920, 2283

* Taken from Singh *et al.* (*Proc. Ind. Acad. Sci.*, 1935, **2A**, 378 ; 1947, **26A**, 268).

The agreement between the values of λ_{max} and λ_o is, thus, very close.

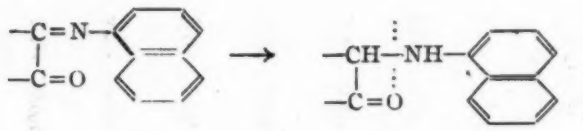
It is therefore clear that there is sufficient evidence to show that the 'characteristic' wave-lengths (λ_o) deduced from Drude's rotatory dispersion equation are in agreement with those obtained by the direct measurements of the 'characteristic' ultraviolet absorption maxima (λ_{max}).

On reduction of the azethenoid group of the arylimino-camphors, the conjugation between the double bonds of this group with those of the carbonyl and the aryl groups is broken, resulting in a new chromophore,

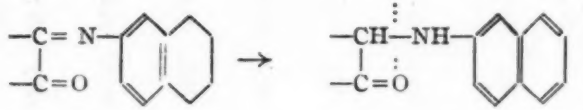


[X]

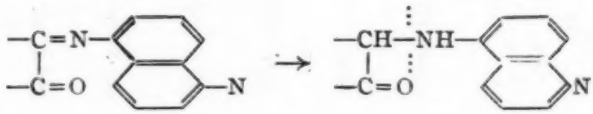
in which the optimum association of double bonds is no longer present. It is accompanied by not only a phenomenal depression of the rotatory powers, as pointed out above, but also by a great fall in the value of λ_o from about 3900 – 4000 Å to about 2800 – 2900 Å, pertaining to the keto group, in the case of phenyl- and chlorophenyl-imino-*d*-camphors. There are also lower 'characteristic' wave-lengths at about 2200 – 2400 and 1734 Å, associated with this chromophore. On the other hand, in the case of naphthyl and quinolino derivatives, the chromophore has the following values of the λ_o:



[λ_o = 3269Å] [λ_o = 3454, 3221Å]



[λ_o = 3523, 3205 Å] [λ_o = 3217 Å]



[λ_o = 3598, 3293 Å] [λ_o = 3464, 3177 Å]

The 'characteristic' wave-lengths (λ_o) associated with the above mentioned chromophores containing the azethenoid linking are lower (3500 − 3600 Å and 3200 − 3300 Å) than those of the chromophores of phenyl- and substituted phenyliminocamphors (3900 − 4000 Å). It must be ascribed to the different aryl groups present in these compounds. On the whole, there is a very small lowering in the 'characteristic' wave-lengths associated with the chromophore of these compounds, when the azethenoid group is replaced by the alkylamino group. The 'characteristic' wave-length of the keto group (λ_o = 2800 − 2900 Å) has disappeared and is replaced by two 'characteristic' wave-lengths at about 3450 and 3200 Å.

FIG. 1

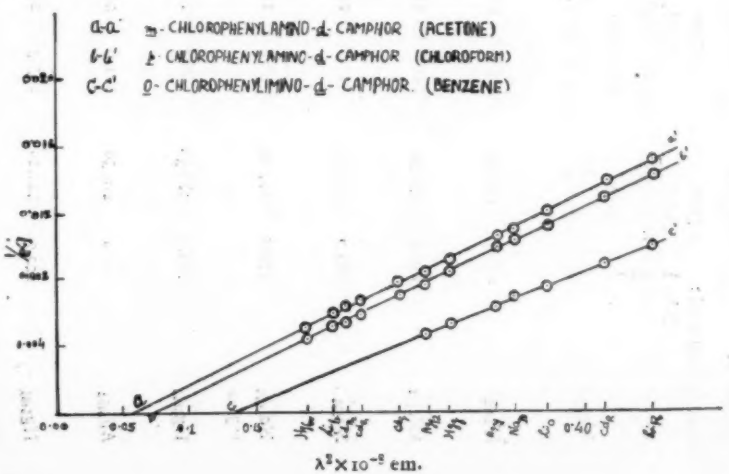


TABLE I

o-Chlorophenylimino-d-camphor.

Solvents:	MeOH.		EtOH.		Acetone.		Pyridine.		EtAc.		$CHCl_3$.		Benzene.	
Conc. (g./100 c.c.):	0.3000		0.3000		0.3000		0.3000		0.3000		0.3000		0.3000	
Calc. $[\alpha] = \frac{43.77}{\lambda^2-0.09947}$			$\frac{35.19}{\lambda^2-0.1251}$		$\frac{41.56}{\lambda^2-0.1342}$		$\frac{49.12}{\lambda^2-0.1367}$		$\frac{40.13}{\lambda^2-0.1059}$		$\frac{38.21}{\lambda^2-0.09523}$		$\frac{31.17}{\lambda^2-0.1329}$	
$\lambda_0 = 0.3152$			0.3536		0.3663		0.3697		0.3254		0.3085		0.3645	
Lines.	[α]. *o*	[α]. *c*	[α]. *o*	[α]. *c*	[α]. *o*	[α]. *c*	[α]. *o*	[α]. *c*	[α]. *o*	[α]. *o*	[α]. *c*	[α]. *o*	[α]. *c*	[α]. *b*
Li_{6708}	125.0	124.89	108.3	108.3	131.6	131.6	155.0	156.8	116.6	116.6	108.3	107.6	98.3	98.3
Cd_{6438}	136.6	138.90	121.6	121.6	148.3	148.2	175.0	176.8	130.0	130.0	120.0	119.7	116.6	110.8
Li_{6104}	160.0	160.03	141.6	142.2	175.0	174.4	208.3	208.3	151.6	150.5	138.3	137.8	131.6	130.1
Na_{5893}	178.3	177.49	158.3	158.4	195.0	195.1	233.3	233.3	166.6	166 3	151.6	151.7	145.0	145.5
Hg_{5780}	186.6	186.56	168.3	168.4	210.0	208.4	250.0	248.8	173.3	175.8	160.0	159.9	155.0	155.0
Ag_{5461}	220.0	219.38	201.6	202.4	251.6	252.2	301.6	302.6	208.3	207.8	188.3	187.5	190.0	187.7
Hg_{5461}	220.0	220.20	203.3	203.3	253.3	253.3	305.0	304.2	208.3	208.3	188.3	188.2	190.0	188.7
Ag_{5200}	255.0	254.67	238.3	240.6	303.3	303.1	365.0	365.0	241.6	242.5	215.0	217.0	223.6	225.3
Cd_{5086}	275.0	275.00	...	...	...	...	...	...	...	...	...	...	...	...

TABLE II

TABLE II

m-Chlorophenylimino-d-camphor.

Solvent:		MeOH.		EtOH.		Acetone.		Pyridine.		EtAc		$CHCl_3$.		Benzene.	
Conc. (g./100 c.c.):		0.3000		0.3000		0.5000		0.5000		0.5000		0.3333		0.5000	
Calc. $[\alpha] = \lambda_e =$		$\frac{78.27}{\lambda^2-0.1563}$ = 0.3953		$\frac{85.55}{\lambda^2-0.1550}$ = 0.3911		$\frac{81.3}{\lambda^2-0.1569}$ = 0.3935		$\frac{84.58}{\lambda^2-0.1789}$ = 0.4241		$\frac{80.41}{\lambda^2-0.1629}$ = 0.4036		$\frac{91.69}{\lambda^2-0.1513}$ = 0.3889		$\frac{94.33}{\lambda^2-0.1541}$ = 0.3925	
Lines.		[α] o	[α] c	[α] o	[α] c	[α] o	[α] c	[α] o	[α] c	[α] o	[α] c	[α] o	[α] c	[α] o	[α] c
Li_{6708}		266.6	266.4	290.0	290.0	278.0	277.4	312.0	312.0	280.0	280.1	307.5	307.0	319.0	318.8
Cd_{6439}		305.0	303.1	331.3	329.7	313.3	314 5	359.0	359.0	320.0	319.7	349.0	348.3	361.0	362.1
Li_{6104}		360.0	361.8	391.6	393.6	378.0	377.1	437.0	436.9	382.0	383.7	414.0	414.5	430.5	431.8
Na_{5893}		410.3	409.9	444.6	445.2	427.0	427.2	502.0	502.5	436.0	436.1	468.0	468.0	490.0	488.4
Ag_{5780}		440.0	439.9	478.0	477.7	459.0	458.7	545.0	545.0	468.2	469.8	500.5	501.6	522.0	520.4
Ag_{5468}		546.6	548.3	593.3	593.9	573.0	572.1	703 0	704.4	590.0	591.0	618.5	620.7	648.0	646.5
Hg_{5462}		553.3	551.4	598.3	597.5	574.8	575.4	710.0	709.1	596.0	594.4	624.0	624.	656.0	654.5
Ag_{5209}		678.3	680.3	735.0	735.7	710.0	710.8	917.0	915.4	745.2	743.5	765.0	764.0	805.0	804.6
Cd_{5086}		748.6	746.6	...	...	...	...	...	...	...	...	...	...	...	...

TABLE III.

p-Chlorophenylimino-d-camphor.

Solvent:	MeOH.		EtOH.		Acetone.		Pyridine.		EtAc.		$CHCl_3$		Benzene.	
Conc. (g./100 c.c.):	0.3000		0.3000		0.4140		0.5000		0.4140		0.4140		0.5000	
Calc. $[\alpha] = \frac{99.5}{\lambda^2-0.1614}$			$\frac{102.74}{\lambda^2-0.1628}$		$\frac{100.86}{\lambda^2-0.1600}$		$\frac{116.6}{\lambda^2-0.1614}$		$\frac{102.2}{\lambda^2-0.1610}$		$\frac{117.82}{\lambda^2-0.1620}$		$\frac{114.4}{\lambda^2-0.1617}$	
$\lambda_0 =$ 0.4017			0.4034		0.4000		0.4017		0.4012		0.4024		0.4021	
Lines.	[α]	[α]	[α]	[α]	[α]	[α]	[α]	[α]	[α]	[α]	[α]	[α]	[α]	[α]
	o	*c*	*o*	*c*	*o*	*c*	*o*	*c*	*o*	*c*	*o*	*c*	*o*	*c*
Li_{6708}	331.6	333.2	358.9	357.5	347.8	347.7	404.0	404.1	353.9	353.7	409.4	408.9	397.0	396.8
Cd_{6438}	391.7	393.1	408.3	408.0	397.2	396.3	463.0	460 8	402.2	403.2	465.0	466.3	453.0	452.5
Li_{6104}	471.6	471.3	490.0	489.7	484.2	485.7	552.0	552.5	484.5	483.3	560.3	559.5	542.0	541.6
Na_{5893}	535.0	535.5	555.8	556.9	538.7	538.5	630.0	627.6	549.8	548.9	635.0	636.5	616.0	616.6
Hg_{5780}	576.6	576.4	600.0	599.8	579.7	579.4	674.0	675.7	591.8	590.5	684.0	684.4	662.0	663.6
Ag_{5468}	723.3	723.1	750.0	754.1	724.8	725.6	842.0	841.4	746.0	744.9	858.2	859.6	833.0	833.2
Hg_{5461}	726.6	727.3	758.0	758.4	729.9	729.8	852.0	852.5	740.1	740.6	865.0	864.8	838.0	838.1
Ag_{5209}	906.2	905.1	946.0	945.2	907.2	906.3	...	...	925.6	926.6	1078.0	1077.0	1044.0	1043.0

TABLE IV

o-Chlorophenylamino-d-camphor.

Solvents:	MeOH.		EtOH.		Acetone.		Pyridine.		EtAc.		$CHCl_3$.		Benzene.	
Conc. (g./100 c.c.):	0.5000		0.5000		1.000		1.000		1.000		1.000		1.000	
Calc. $[\alpha] = \frac{}{\lambda^2}$	$\frac{15.84}{\lambda^2-0.0979}$		$\frac{20.076}{\lambda^2-0.0712}$		$\frac{21.65}{\lambda^2-0.07705}$		$\frac{16.05}{\lambda^2-0.08535}$		$\frac{24.76}{\lambda^2-0.06628}$		$\frac{24.71}{\lambda^2-0.0718}$		$\frac{15.57}{\lambda^2-0.0878}$	
$\lambda_e =$	0.3128		0.2668		0.2775		0.2921		0.2574		0.2679		0.2963	
Lines	[α] *o*	[α] *c*	[α] *o*	[α] *c*	[α] *o*	[α] *c*	[α] *o*	[α] *c*	[α] *o*	[α] *c*	[α] *o*	[α] *c*	[α] *o*	[α] *c*
Li_{6708}	45.0	45.00	53.0	52.98	58.0	58.05	44.0	44.00	64.5	64.52	65.5	65.49	43.0	42.99
Cd_{6438}	50.0	50.03	59.0	58.45	64.5	62.32	49.0	48.74	72.0	71.09	72.5	72.28	48.5	47.66
Li_{6104}	57.0	57.69	66.0	66.61	73.0	72.78	56.0	55.58	81.0	80.85	83.0	82.37	54.5	54.69
Na_{5893}	64.0	63.54	73.0	72.71	80.5	80.13	61.5	61.28	87.5	88 14	90.0	89.95	60.0	60.02
Hg_{5780}	67.0	67.07	77.0	76.33	83.5	84.22	64,5	64.49	92.5	92.43	93.5	94.43	64.0	63.32
Ag_{5616}	79.0	78.77	88.0	88.10	99.0	97.52	75.0	75.09	105.0	106.40	110.5	109 00	72.5	73.72
Hg_{5461}	79.0	79.11	87.0	88.41	98.0	97.78	75.0	75.39	106.5	106.80	109.5	109.40	73.5	73.98
Ag_{5209}	91.0	91.37	102.0	100.30	112.5	111.40	87.0	86.28	122.5	120.70	125.5	124.20	85.0	84.84
Cd_{5086}	98.0	98.60	108.0	107.10	118.5	119.20	92.0	92.54	128.0	128.70	132.5	132.60	91.0	91.80
Cd_{4799}	118.0	119.60	128.0	126.10	143.0	141.10	10.01	110.06	149.5	150.90	158.0	156.20	108.5	109.10
Cd_{4678}	131.0	131.10	136.0	135.90	150.5	152.70	119.5	120.10	161.0	162.30	170.0	168.50	120.0	118.80
Li_{4603}	140.0	139.10	143.0	142.80	162.5	160.60	128.5	126.90	170.0	170.00	177.0	906.70	123.5	125.16
Hg_{4358}	172.0	172.00	168.0	168.90	191.5	191.60	152.5	153.30	200.0	200.00	209.5	209.50	152.0	152.40

TABLE V

m-*Chlorophenylamino-d-camphor.*

Solvents:	MeOH.		EtOH.		Acetone.		Pyridine.		EtAc.		$CHCl_3$		Benzene.	
(Conc. g./100 c.c.):	1.000		1.000		1.000		1.000		1.000		1.000		1.000	
Calc. $[\alpha]_{\lambda_0}$ =	$\frac{25\,815}{\lambda^2-0.04665}$		$\frac{25.56}{\lambda^2-0.05964}$		$\frac{25.76}{\lambda^2-0.05671}$		$\frac{9\,69}{\lambda^2-0.0911}$		$\frac{29.94}{\lambda^2-0.05725}$		$\frac{28.34}{\lambda^2-0.09367}$		$\frac{26.55}{\lambda^2-0\,08826}$	
=	0.2159		0.2442		0.23807		0.3017		0.2392		0.30605		0.29708	
Lines.	[α]. *o*	[α]. *c*	[α]. *o*	[α]. *c*	[α]. *o*	[α]. *c*	[α]. *o*	[α]. *c*	[α]. *o*	[α]. *c*	[α]. *o*	[α]. *c*	[α]. *o*	[α]. *c*
Li_{6708}	64.0	64.01	65.5	65 46	65.5	65.49	27.0	29.00	76.0	76 19	79 5	79.51	73.5	73.4
Cd_{6438}	70.0	70.17	72.0	72.01	71.5	71.97	29.5	29.96	83.0	83.79	87.6	88.35	81.0	81.37
Li_{6104}	79.0	79.21	82.0	81.68	82.0	81.56	34.5	34.43	95.0	94.95	102.0	101.60	93.5	93.42
Na_{5893}	86.0	85.88	89.5	88 65	89.0	88.67	38.0	37.84	103.5	103.20	112.5	111.90	102.5	102.50
Hg_{5780}	90.0	89.78	94.0	93.09	93.0	92.85	40.0	39.87	107.5	108.50	117.5	117.90	107.0	108.00
Ag_{5469}	102.0	102.30	105.5	105.30	106.0	106,30	46.5	46.37	123.0	123.50	138.0	138.00	126.0	126 00
Hg_{5461}	103.0	102.60	107.0	107.10	107.5	106.70	46.5	46.78	123.5	124 30	139.0	138.60	126.5	126 50
Ag_{5209}	115.0	114.90	121.0	120.70	120.0	120.00	52.0	53.70	141.0	139.80	159.0	159.50	144 0	145.10
Cd_{5086}	122.0	121.80	128.5	128.30	126,5	127.60	56.5	57.81	149,0	148.70	169.5	171.80	155.0	155 90
Cd_{4799}	141.0	141.40	150.5	149.60	149.0	148.40	70.0	69.55	172 0	173.00	207.4	206.00	188.5	186.80
Cd_{4678}	148.0	149.90	159.5	160.40	157.0	158.90	76.5	75.80	184.5	185.20	225.0	226.60	201.5	203.40
Li_{4603}	158.0	156.30	166.0	167.90	165.2	166.10	82,0	80.34	192.5	193.70	240,0	240.00	215.0	215.00
Hg_{4358}	180.0	180 20	196.0	196.01	193.5	193 20	98.0	97.97	225.5	225.50	294.1	294.30	260.0	261.00

TABLE VI

p-*Chlorophenylamino*-d-*camphor*.

Solvents:	MeOH.		EtOH.		Acetone.		Pyridine.		EtAc.		$CHCl_3$.		Benzene.	
Conc. (g./100 c.c.):	0.5000		0.5000		1.0000		1.0000		1.0000		1.0000		1.0000	
Calc. [α] =	$\frac{24.784}{\lambda^2-0.0301}$		$\frac{24.42}{\lambda^2-0.04965}$		$\frac{24.570}{\lambda^2-0.0600}$		$\frac{12.206}{\lambda^2-0.07425}$		$\frac{23.58}{\lambda^2-0.0762}$		$\frac{26.04}{\lambda^2-0.0577}$		$\frac{25.85}{\lambda^2-0.08366}$	
λ_0 =	0.1734		0.2228		0.2449		0.2724		0.2766		0.2402		0.2893	
Lines.	[α]. *o*	[α]. *c*	[α]. *o*	[α]. *c*	[α]. *o*	[α]. *c*	[α]. *o*	[α]. *c*	[α]. *o*	[α]. *c*	[α]. *o*	[α]. *c*	[α]. *o*	[α]. *c*
Li_{6708}	59.0	59.02	61.0	61.01	62.99	62.99	32.5	32.53	63.0	63.10	69.5	69.60	70.5	70.57
Cd_{6438}	65.0	64.46	67.0	66.85	70.99	69.31	36.5	35.93	69.5	69.71	77.0	77.02	78.5	78.16
Li_{6104}	73.0	72.38	76.0	75.65	79.50	78.61	41.0	40 99	79.0	79.60	88.0	87.78	89.5	89.50
Na_{5893}	79.0	78.14	82.0	82.10	84.00	85.50	45.0	44.78	87.0	87.02	96.0	95.96	98.0	98.11
Hg_{5790}	81.0	81.49	85.0	85.88	88.50	89 66	46.5	47.03	90.2	89.00	99.0	100.80	103.2	102.50
Ag_{5168}	93.0	92.15	98.0	97.97	102.00	102.80	54.0	54.39	105.0	105.90	118.0	116.70	120.0	120.00
Hg_{5461}	93.0	92.43	98.0	98.25	104.00	103.10	54.5	54.39	105.0	106.20	119 0	117.10	121.0	120.50
Ag_{5039}	102.0	102.80	110.0	110.30	115.50	116.20	62.5	62.03	119.5	120.90	135.0	133.20	137.5	137.80
Cd_{5086}	109.0	108.40	115.0	116.90	124.60	123.70	65.5	66.28	129.5	129.30	143.0	142.50	148.5	147.90
Cd_{4799}	123.0	123.80	137.0	135.20	145.00	144.30	76.0	78.39	152.0	153.00	169.0	168.50	177.5	176.20
Cd_{4678}	131.0	131.30	146.0	144.40	153.00	154.70	83.0	84.50	167.0	165.50	184.5	182.00	193.0	191.40
Li_{4603}	140.0	136.40	152 0	150.70	160.50	161.80	88.5	89.54	174.0	174.00	195.0	191.50	202.5	201.80
Hg_{4358}	155.0	155.00	174.0	174.10	189.00	189.00	105.5	105.60	208.5	207.20	228.0	228.30	243.0	243.20

TABLE VII

Phenylamino-d-camphor.

Solvents:	MeOH.		EtOH.		Acetone.		Pyridine		EtAc.		$CHCl_3$		Benzene.	
Conc. (g./100 c.c.):	0.5000		0.5000		1.000		1.000		1.000		1.000		1.000	
Calc. $[\alpha]_{\lambda_0}$ =	$\frac{27.48}{\lambda^2-0.05741}$		$\frac{28.66}{\lambda^2-0.05735}$		$\frac{28.51}{\lambda^2-0.06469}$		$\frac{14.132}{\lambda^2-0.08389}$		$\frac{25.796}{\lambda^2-0.09173}$		$\frac{31.3}{\lambda^2-0.0796}$		$\frac{31.15}{\lambda^2-0.07015}$	
=	0.2348		0.2395		0 2543		0.2896		0.3028		0.2821		0.2648	
Lines.	[α]. *o*	[α]. *c*	[α]. *o*	[α]. *c*	[α]. *o*	[α]. *c*	[α]. *o*	[α]. *c*	[α]. *o*	[α]. *c*	[α]. *o*	[α]. *c*	[α]. *o*	[α]. *c*
Li_{6708}	70.0	70.0	73.0	72.98	74.0	73.99	38.5	38.59	72.0	71.99	84.5	84.50	82.0	82.06
Cd_{6438}	77.0	76.96	80.0	80.27	80.5	81.50	43.5	42.74	78 5	79.91	94.0	93.43	90.0	90.46
Li_{6104}	88.0	87.24	89.0	90.93	94.0	92.64	50.0	48.96	92.5	91.87	108.5	106.80	104.0	103.0
Na_{5893}	96.0	94.84	99.0	98.86	100.5	100.9	54.0	53.56	101.0	100.9	118.5	116.9	112.0	112.5
Hg_{5780}	100.0	99.33	104.0	103.5	105.5	105.8	56.5	56.48	105.5	106 4	123.0	123.0	118.5	118.0
Ag_{5468}	116.0	113.8	119.0	118.6	122,5	121.7	66.5	65.69	124.5	124.5	142.0	142.7	137.5	136.0
Hg_{5461}	115.0	114.0	119.0	119.0	121.0	122.1	65.5	65.94	124.5	124.9	143.0	143.2	137.0	136.7
Ag_{5209}	126.0	125.6	134.0	134.0	140.0	138.0	75.5	75.41	144.0	143.6	163.5	163.3	155.0	154.9
Cd_{5086}	135.0	136.7	143.0	142.4	149.5	147.0	81.5	80.89	154.0	154.5	176.0	174.9	163.5	165.4
Cd_{4799}	157.0	159.0	165.0	165.6	172.5	172.1	95.5	96.42	188.5	186.1	209.0	207.6	194.5	194.5
Cd_{4678}	169.0	170.3	177.0	177.5	186.5	185.0	104.5	104.70	203.5	203.0	225.0	224.7	207.5	209.6
Li_{4603}	178.0	178.0	185.0	185.6	193.5	193.8	110.5	110.50	215.0	214.8	237.0	236.8	218.5	220.1
Hg_{4358}	209.0	207 3	216.0	216.0	227.5	227.6	134.5	133.10	261.5	262.2	283.5	286.6	261.0	260.0

We reserve the work of correlating the 'characteristic' wave-lengths (λ_o) deduced from optical rotatory dispersion equations of Drude and the 'characteristic' ultraviolet absorption maxima (λ_{max}) by direct measurements.

EXPERIMENTAL

These compounds were prepared and purified according to the methods described by us (Singh and Seth, this *Journal*, 1956, **33**, 491). The rotatory dispersion determinations were made at 35° in seven solvents for 13 wave-lengths of the visible spectrum (λ = 6708Å to 4358Å) and are recorded in Tables I-VII. The values of λ_o, calculated from the dispersion formulae, are also recorded in the tables and are expressed as μ or 10^{-4} cm.

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AMINO DERIVATIVES OF TITANIUM TETRABROMIDE. PART I

By Sarju Prasad and Jai Baniprasad Tripathi

The amino derivatives of titanic bromide have been prepared by the action of titanium tetrabromide on some mono- and di-amines, their properties studied and structures discussed.

The co-ordination number of titanium is six, but compounds in which titanium has co-ordination number of four and eight have also been reported in the literature. Ruff and Eisner (*Ber.*, 1998, **41**, 2260) studied the action of ammonia gas on titanium tetrabromide at a low temperature and obtained titanium octaminotetrabromide, $TiBr_4.8NH_3$. Rosenheim and Schütte (*Z. anorg. Chem.*, 1901, **26**, 239) saturated a solution of pyridine hydrobromide and titanic acid in alcoholic hydrobromic acid with hydrogen bromide and isolated pyridino-bromotitanic acid, $(C_6H_5N)_2.H_2TiBr_6$.

The present investigation was undertaken with a view to studying the formation of compounds by treating titanium tetrabromide with aromatic primary amines in ether.

Experimental

The amines used were of Merck's or B.D.H. 'extra pure' quality. Ether was distilled over metallic sodium. Titanium tetrabromide was prepared by the method of Olsen and Ryan (*J. Amer. Chem. Soc.*, 1932, **54**, 2215), redistilled at 230° and extracted with ether.

General Method of Preparation.—A dilute solution of the amine, prepared in anhydrous ether, was slowly added to the titanium tetrabromide solution with constant stirring. When just the requisite quantity of the amine solution had been added, the reddish yellow colour of the bromide solution was discharged and the supernatant liquid became colorless. The amine solution was then added in slight excess and left for about an hour. The precipitate was filtered and washed with anhydrous ether till the washings did not form any precipitate with titanium tetrabromide. It was dried at the room temperature, analysed and its properties studied. Two sets of experiments were carried out simultaneously. The results reported in Tables I and II are the average of the two values.

Table I

Compounds of titanium tetrabromide with primary diamines.

Amine.	Compounds.	Colour.	M.P.	% Titanium.		% Bromine.		% Nitrogen.	
				Found.	Calc.	Found.	Calc.	Found.	Calc.
Benzidine	Dibenzidino-TB $[Ti(NH_2C_6H_4\text{-}C_6H_4NH_2)_2]Br_4$	Light ash-grey	>400°	6.54	6.51	43.44	43.46	7.60	7.61
o-Tolidine	Di-*o*-tolidino-TB $[Ti(CH_3NH_2C_6H_3\text{-}C_6H_3NH_2.CH_3)_2]Br_4$	Light reddish brown	,,	6.08	6.05	40.39	40.39	7.03	7.07
o-Phenylene-diamine	Di-*p*-phenylene-TB diamino-TB $[Ti\{C_6H_4(NH_2)_2\}_2]Br_4$	Greyish black	,,	8.26	8.21	54.72	54.78	9.57	9.60
Dianisidine	Di-dianisidino-$[Ti\{CH_3O.(NH_2)C_6H_3\text{-}C_6H_3(NH_2)OCH_3\}_2]Br_4$	Purple	,, 120°	5.64	5.60	37.34	37.36	6.56	6.55
o-Naphthylene diamine	Di-*o*-naphthylene diamino-TB $[Ti\{C_{10}H_6(NH_2)_2\}]Br_4$	Deep crimson red	(decomp.) 268°	7.02	7.01	46.76	46.77	8.22	8.19

TABLE II

Compounds of titanium tetrabromide with primary monoamines.

[TB denotes titanic bromide]

Amine.	Compound formed.	Colour.	M.P.	% Titanium.		% Bromine.		% Nitrogen.	
				Found.	Calc	Found.	Calc.	Found.	Calc.
Aniline	Tetranilino-TB $[Ti(C_6H_5NH_2)_4]Br_4$	White	280°	6.51	6.48	43.20	43.22	7.53	7.57
o-Toluidine	Tetra-*o*-toluidino-TB $[Ti(CH_3C_6H_4NH_2)_4]Br_4$	,,	221°	6.01	6.02	40.15	40 18	7.06	7.04
m-,,	Tetra-*m*-toluidino-TB $[Ti(CH_3C_6H_4NH_2)_4]Br_4$	Light pink	243°	6.03	6.02	40.18	40.18	7.02	7.04
o-Anisidine	Tetra-*o*-anisidino-TB $[Ti(CH_3O.C_6H_4NH_2)_4]Br_4$	White	282°	5.56	5.57	37.15	37.20	6.48	6.51
o Phenetidine	Tetra-*o*-phenetidino-TB $[Ti(C_2H_5O.C_6H_4NH_2)_4]Br_4$	Dirty white	188°	5.25	5.23	34.88	34.92	6.10	6.12
p- ,,	Tetra-*p*-phenetidino-TB $[Ti(C_2H_5O.C_6H_4NH_2)_4]Br_4$	Light ash	285° (decom.)	5.23	5.23	34.86	34.92	6.14	6.12
Benzylamine	Tetrabenzylamino-TB $[Ti(C_6H_5CH_2.NH_2)_4]Br_4$	White	226°	6.05	6.02	40.14	40.18	7.02	7.04
p-Toluidine	Tetra-*p*-toluidino-TB $[Ti(CH_3C_6H_4NH_2)_4]Br_4$	Light yellow	302°	6.02	6.02	40.16	40.18	7.04	7.04
α-Naphthyl-amine	Tetra-α-naphthyl-amino-TB $[Ti(C_{10}H_7NH_2)_4]Br_4$	Dirty white	297°	5.12	5.10	34.00	34.02	5.98	5.96
β-Naphthyl-amine	Tetra-β-naphthyl-amino-TB $[Ti(C_{10}H_7NH_2)_4]Br_4$	Pinkish white	265°	5.14	5 10	34.01	34.02	5.97	5.96
p-Anisidine	Tetra *p* ansidino-TB $[Ti(CH_3O.C_6H_4NH_2)_4]Br_4$	Dirty white	320° (decomp.)	5 60	5.57	37.16	37.20	6.50	6.51

Bromine was estimated by Piria and Schiff's method, nitrogen by Kjeldahl's method and titanium as TiO_2.

DISCUSSION

The effective atomic number of titanium in both the series of compounds is 26, which is not a stable configuration, and therefore the compounds, though stable at the room temperature, begin to hydrolyse slowly as soon as they come in contact with water or other reagents, e.g. sodium hydroxide, sodium carbonate, etc. The compounds with mono-amines hydrolyse slowly at the room temperature but rapidly when heated to 50°, and $Ti(OH)_4$ is precipitated according to the equations:

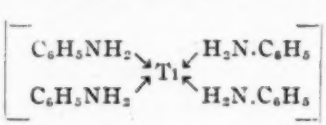
$$Ti\ (4\ Am)\ Br_4 + 4H_2O = Ti\ (OH)_4 + 4\ Am.\ HBr$$

$$Ti\ (4\ Am)\ Br_4 + 4NaOH = Ti\ (OH)_4 + 4NaBr + 4\ Am,$$

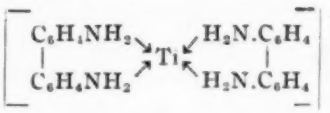
whereas those with the diamines are more stable and hydrolyse slowly even on boiling.

On heating alone they furnish a white, greyish white or grey sublimate, soluble in water, acidic and responding to tests for Br and NH_2. The compounds with mono-amines afford this sublimate at lower temperatures than those with the diamines. When they are heated with soda-lime the corresponding amines separate out and condense in the cooler part of the tube. All the compounds respond to the diazo test.

It appears that the amines attach themselves to the central atom, chelate compounds being formed in the case of diamines, which is responsible for the greater stability of these compounds, and may be represented as :



in the case of a mono- amine, such as aniline, and the chelate compounds of the structure :



in the case of a diamine such as benzidine.

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ON THE STABILITY OF INNER-METALLIC COMPLEXES

By Basudeb Das Sarma and Priyadaranjan Rây

A detailed study of the mechanism of formation and dissociation of a series of copper and nickel biguanide complexes has been made in aqueous solution. The variations of the acid-dissociation constants of the ligand with substitution against the change in the stability of the respective complexes have been discussed. The results are compatible with a single-step dissociation for the Ni *bis*-biguanides and Cu and Ni dibiguanides as compared to the distinct two-step dissociation of the Cu *bis*-biguanide complexes.

A detailed study of the mechanism of formation and stability of co-ordination complexes was initiated mainly by N. Bjerrum and his school with the observation that the formation of complex ions always occurred stepwise. The problem of complex formation has been treated on a statistical basis by J. Bjerrum ("Metal ammine formation in aqueous solution", P. Haase and Sons, Copenhagen, 1941), involving all the possible intermediate stages in a reversible manner.

Bjerrum's method has been successfully employed to the case of inner-metallic complexes by Calvin and Wilson (*J. Amer. Chem. Soc.*, 1945, **67**, 1334), Mellor *et al.* (*ibid.*, 1948, **70**, 401), Ackerman *et al.* (*Nature*, 1949, **168**, 723) and others.

Inner-metallic complexes of higher order, formed by biguanidine molecules as ligands with metal ions like Cu, Ni, Co, Ag and Pd, have been the subject matter of investigation by P. Rây and co-workers in this laboratory for the last few years. These form very convenient starting materials for a quantitative survey of the nature and stability of inner-metallic complexes in as much as the ligands and the complex chlorides, formed by them, are, as a rule, freely soluble in water and are easily obtainable in the pure solid state. A study of the mechanism of decomposition of these complexes and of their relative stabilities constitute the purpose of the present investigation.

The biguanide complex of bipositive metals reacts with acids in aqueous solution in the following way :

$$\left.\begin{aligned}[M(BigH)_2]^{2+} + [H^+] &\rightleftharpoons [M(BigH)]^{2+} + [BigH_2]^+ \\ [M(BigH)]^{2+} + [H^+] &\rightleftharpoons [M]^{+} + [BigH_2]^+\end{aligned}\right\} \quad \ldots (1)$$

where M is a bivalent metal ion like Cu^{2+} or Ni^{2+} and BigH and $BigH_2^+$ represent respectively the biguanide base and biguanidinium ion corresponding to the uptake of a proton.

The equilibrium constants of the reactions (1) are given by

$$k'_2 = \frac{[M(BigH)]^{2+}\,[BigH_2]^+}{[M(BigH)_2]^{2+}\,[H^+]}$$

$$k'_1 = \frac{[M]^{2+}\,[BigH_2]^+}{[M(BigH)]^{2+}\,[H^+]} \quad \ldots \quad \ldots (2)$$

These are related to the successive instability or dissociation constants, k_1 and k_2, in the following way :

$$k_2 = \frac{[M(BigH)]^{2+}}{[M(BigH)_2]^{3+}} \quad [BigH] = \frac{[M(BigH)]^{2+}}{[M(BigH)_2]^{3+}} \cdot \frac{[BigH_2]^{+}}{[H^+]} \cdot \frac{[H^+]\,[BigH]}{[BigH_2]^{+}}$$

$$= k'_2.k_1^* \text{ ; similarly } k_1 = k'_1.k_1^* \qquad \ldots \quad (3)$$

where k^*_1 is the first acid-dissociation constant of the co-ordinated ligand, from

$$BigH_2^+ \rightleftharpoons BigH + H^+.$$

The determination of the acid-dissociation constants of the biguanide bases has been described in a previous communication (this *Journal*, 1952, **29**, 217).

The experimental technique employed for the determination of k'_1 and k'_2 was simpler and was more straight forward than those adopted by earlier workers. Evaluation of k'_1 and k'_2 was made from a measurement of the p_H values of the equilibrium mixture of a known amount of the complex and definite volumes of standard acid of widely varying strengths at a constant temperature.

The complex salts employed were the hydrochlorides, due to their reasonably high solubility, and the acid used was hydrochloric acid.

Formation of any chloro-complex of copper and nickel in appreciable amounts may be neglected in the light of the works of Carlson (*J. Amer. Chem. Soc.*, 1945, **67**, 1334) and also of Sockelberg and Freyhold (*Z. Elektrochem.*, 1940, **46**, 120).

The calculation is made as follows :

Let X = total concentration of non-complex-bound biguanide liberated at equilibrium. Then

$$X = BigH + BigH_2^+ + BigH_2^{2+}$$

$$= BigH_2^+ \left(\frac{k_1^*}{H^+} + 1 + \frac{H^+}{k_2^*}\right)$$

$$= BigH_2^+ \left(\frac{k_1^* k_2^* + k_2^* H^+ + [H^+]^2}{k^*_2\, H^+}\right) \quad \ldots \quad \ldots \quad (4)$$

Let Z = acid consumed in the process at equilibrium by the reaction of the added acid with the complex, obtained from the initial p_H of the acid and the final p_H values of the solution mixture and the p_H-acid relation graph. Then

$$Z = C_H - C'_H$$

(where C_H and C'_H represent respectively concentration of the total acid added and of that present at equilibrium derived from the observed p_H and the acid-p_H relation)

$$= BigH_2^+ + 2\,BigH_3^{2+}$$

$$= BigH_2^+ \left(1 + \frac{2H^+}{k^*_2}\right) \quad \ldots \quad \ldots \quad (5)$$

(acid liberated by the reaction $BigH = Big^- + H^+$ being negligible in solution of $p_H < 9$).

From (4) and (5)

$$BigH_2^+ = \frac{Z.\,k_2^*}{k_2^* + 2H^+} \qquad \text{and}$$

$$X = \frac{Z.(k_1^*.k_2^* + k^*_2 H^+ + [H^+]^2)}{k_2^* H^+ + 2[H^+]^2} \quad \ldots \quad \ldots \quad (6)$$

Let the concentration of the complex taken = C and at equillibrium

$$[M(BigH)_2]^{2+} = C_2$$
$$[M(BigH)]^{2+} = C_1$$

$$[M^{2+}] = C_0 \text{ and } \frac{[BigH_2]^+}{[H^+]} = [b]$$

Then $$C = C_2 + C_1 + C_0 \quad \ldots \quad \ldots \quad (7)$$

When $X < C$, C_0 is negligible or $C = C_2 + C_1$;

$$C_1 = X \text{ and } C_2 = C - X$$

giving from (2), $$k'_2 = \frac{X}{C - X} \cdot b \quad \ldots \quad \ldots \quad (8)$$

Again, when $X > C$, but $< 2C$, C_2 is negligible, and $C = C_1 + C_0$, $C_1 = 2C - X$ and $C_0 = X - C$, whence,

$$k'_1 = \frac{X - C}{2C - X} \cdot [b] \quad \ldots \quad \ldots \quad (9)$$

The relation between $\bar{n}$ and log $([BigH_2^+]/[H^+]) = \log [b]$ may be plotted in a graph, where $\bar{n}$ = average number of biguanide molecules attached to a metal ion. Then

$$\bar{n} = \frac{C_1 + 2C_2}{C_0 + C_1 + C_2} = \frac{2C - X}{C} \quad \ldots \quad \ldots \quad (10)$$

substituting for C_1, C_2 etc. from (8) and (9)

$$\bar{n} = \frac{k'_2.[b] + 2[b]^2}{k'_1.k'_2 + k'_2.b + [b]^2} \quad \ldots \quad \ldots \quad (11)$$

which can be written as

$$k'_1 = [b]\frac{1 - \bar{n}}{\bar{n}} + \frac{2 - \bar{n}}{\bar{n}} \cdot [b]^{2+} \quad \ldots \quad \ldots \quad (12)$$

Again, when $\bar{n} = n - \frac{1}{2}$, the concentration of MA_n and MA_{n-1} becomes practically equal and $k'_n = [b]'_{n=n-\frac{1}{2}}$ to a first approximation from equation (12)

$$k'_1 = [b]_{n=\frac{1}{2}} \cdot \left(2 + \frac{3}{k_2} \cdot [b]_{n=\frac{1}{2}}\right)$$

and $$k'_2 = [b]_{n=3/2} \cdot \left(\frac{[b]_{n=3/2}}{3k'_1 + [b]_{n=3/2}}\right)$$

From which the values of k'_1 and k'_2 may be accurately obtained, whence equation (3) gives the successive instability constants.

The stability of a few of these complexes was also determined from a study of their formation from metal ions and the biguanide salt solutions, which give rise to the complexes $M(BigH)^{2+}$ and $M(BigH)_2^{2+}$, depending upon the p_H of the mixture. Thus,

$$\left.\begin{aligned} M^{2+} + BigH_2^+ &\rightleftharpoons M(BigH)^{2+} + H^+ \quad \ldots \\ M(BigH)^{2+} + BigH_2^+ &\rightleftharpoons M(BigH)_2^{2+} + H^+ \quad \ldots \end{aligned}\right\} \quad \ldots \quad (13)$$

whence, $k'_{f_1} = \frac{C_1}{C_0} \cdot \frac{1}{[b]} = \frac{1}{k'_1}$ and

$$k'_{f_2} = \frac{C_2}{C_1} \cdot \frac{1}{[b]} = \frac{1}{k'_2}$$

where k'_{f1} and k'_{f2} are related to the formation constants of the system and C_0, C_1, C_2 and $[b]$ have their usual significance.

Let C_A = total biguanide added, A_c = biguanide in complex and A_n = not complex-bound biguanide

C_M = total metal concentration.

Z = acid liberated in the reaction.

C'_H = acid concentration in the final mixture.

C_H = acid concentration of the component solutions before mixing.

C_H' = acid equivalent of the alkali added.

Now $Z = C_H' - C_H + C'_H$ and

$$C_A = A_c + A_n = A_c + BigH_3^{2+} + BigH_2^{+} + BigH$$

$$= A_c + BigH_2^{+} \cdot \left(\frac{H^+}{k_2^*} + 1 + \frac{k_1^*}{H^+} \right) \quad \ldots \quad \ldots \quad (14)$$

and $Z = A_c + BigH - BigH_3^{2+}$

$$= A_c + BigH_2^{+} \left(\frac{k_1^*}{H^+} - \frac{H^+}{k_2^*} \right) \quad \ldots \quad \ldots \quad (15)$$

From (14) and (15),

$$BigH_2^{+} = \frac{(C_A - Z)\, k_2^*}{k_2^* - 2H^+} \quad \ldots \quad \ldots \quad (16)$$

$$\text{And } A_c = Z - \frac{(C_A - Z)\,(k_1^* . k_2^* - [H^+]^2)}{H^+ . k_2^* + 2[H^+]^2} \quad \ldots \quad (17)$$

when $A_c < C_M$, C_2 is negligibly small.

$$C_M = C_0 + C_1$$
$$A_c = C_1 ; \; C_0 = C_M - A_c$$

$$\text{giving } k'_{f_1} = \frac{C_1}{C_0} \cdot \frac{1}{[b]} = \frac{A_c}{C_M - A_c} \cdot \frac{1}{[b]} \quad \ldots \quad \ldots \quad (18)$$

Again when $A_c > C_M$, but $< 2\, C_M$, C_0 is negligibly small, Hence

$$C_M = C_1 + C_2 \text{ and } A_c = C_1 + 2C_2$$
$$C_2 = A_c - C_M ; \; C_1 = 2C_M - A_c$$

$$\text{giving } k'_{f_2} = \frac{C_2}{C_1} \cdot \frac{1}{[b]} = \frac{A_c - C_M}{2C_M - A_c} \cdot \frac{1}{[b]} \quad \ldots \quad \ldots \quad (19)$$

The decomposition mechanism of dibiguanide complexes can be satisfactorily represented by a single-step process found from the present physico-chemical study, in the following form :

$$M(A)^{2+} + 2H^+ \rightleftharpoons M^{2+} + AH_2^{2+} \quad \ldots \quad \ldots \quad (20)$$

where M is a bivalent metal ion like Cu^{2+} or Ni^{2+}, and A represents a molecule of a dibiguanide base, while AH_2^{2+} is the dibiguanidinium ion corresponding to the uptake of two protons.

The equilibrium constant of (20) is given by

$$K' = \frac{M^{2+}.AH_2^{+}}{MA^{2+}.[H^+]^2} \quad \ldots \quad \ldots \quad (21)$$

As before, if X and Z represent the total biguanide liberated and the acid consumed in the process at equilibrium respectively,

$$X = A + AH^+ + AH_2^{2+} + AH_3^{3+} + AH_4^{4+}$$

$$X = AH_2^{2+}\left[\frac{k_1^* k_2^*}{[H^+]^2} + \frac{k_2^+}{H^+} + 1 + \frac{H^+}{k_3^*} + \frac{[H^+]^2}{k_3^* k_4^*}\right] \quad \ldots \quad (22)$$

where k_1^*, k_2^*, k_3^* and k_4^* are the successive acid-dissociation constants of the dibiguanide.

And $Z = C_H - C'_H = AH^+ + 2AH^{2+} + 3AH_3^{3+} + 4AH_4^{4+}$

$$= AH_2^{2+}\left[\frac{k_2^*}{[H^+]} + 2 + 3.\frac{[H^+]}{k_1^*} + \frac{4[H^+]^2}{k_3^* k_4^*}\right] \quad \ldots \quad \ldots \quad (23)$$

From (22) and (23),

$$[AH_2]^{2+} = \frac{Z.[H^+].k_3^* k_4^*}{k_2^* k_3^* k_4^* + 2[H^+].k_3^* k_4^* + 3[H^+]^2.k_1^* + 4[H^+]^3}$$

$$X = \frac{Z}{[H^+]} \cdot \frac{k_1^* k_2^* k_3^* k_4^* + [H^+]k_2^* k_3^* k_4^* + [H^+]^2.k_3^* k_4^* + [H^+]^3.k_4^* + [H^+]^4}{k_2^* k_3^* k_4^* + 2[H^+].k_3^* k_4^* + 3[H^+]^2.k_1^* + 4[H^+]^3} \quad (24)$$

Let C = concentration of total complex taken,

C_0 = metal ion in solution at equilibrium = M^{2+} and

C_2 = concentration of complex ion in solution at equilibrium. Then

$$C = C_2 + C_0$$

$X = M^{2+} = C_0$ and $C - X = C_2$, giving

$$K' = \frac{[M^{2+}]}{[MA]^2} \cdot \frac{[AH_2^{2+}]}{[H^+]^2} = \frac{C_0}{C_2} \cdot [b] = \frac{X}{C - X} \cdot [b] \quad \ldots \quad (25)$$

where $[b] = [AH_2]^{2+}/[H^+]^2$

As usual the decomposition curve is obtained by plotting $\bar{n}$ and log $[b]$ where

$\bar{n}$ = average number of ligands attached per metal ion,

$$= \frac{\text{complex-bound ligand}}{\text{total metal conc.}} = \frac{C - X}{C} \quad \ldots \quad \ldots \quad (26)$$

Again, from (5),

$$\bar{n} = \frac{[MA]^{2+}}{[M]^{2+} + [MA]^{2+}} = \frac{[M]^{2+}.[b]/K'}{[M]^{2+} + [M]^{2+}.[b]/K'} = \frac{[b]}{K' + [b]} \quad (27)$$

or $K' = (1 - \bar{n}/\bar{n}).[b]$ *i.e.* $K' = [b]_{\bar{n}=1/2}$ ... ... (28)

The instability constant K is then obtained from the equilibrium constant K', using the expression :

$$K = K'.\ k^*_1.k^*_2 \quad \ldots \quad \ldots \quad (29)$$

where k^*_1 and k^*_2 are the first two acid-dissiociation constants of the ligand.

EXPERIMENTAL

The method of preparation of the N-alkyl biguanide complexes is essentially similar, viz., heating under pressure a mixture of copper sulphate, dicyandiamide and the corresponding amine in aqueous solution. The resulting solution on cooling yields the complex sulphate, which forms the starting material for the preparation of the biguanide and its complex copper and nickel chlorides.

TABLE I

	Compound.	References.	Calculated.			Found.		
			% Cu.	% N.	% Cl.	%Cu.	% N.	% Cl.
1.	Copper *bis*-biguanide chloride $Cu(C_2N_5H_7)_2\ Cl_2.2H_2O$.	Ray & Bagchi, this *Journal*, 1939, **16**, 617	17.07	37.57	19.06	17.10	37.52	19 09
2.	Copper *bis*-methyl-biguanide chloride $Cu(C_3H_9N_5)_2\ Cl_2\ 2.5H_2O$.	Reibenschutt, *Monatsch.*, 1883, **4**, 394.	15.52	34 15	17 43	15.99	34.21	17 49
3.	Copper *bis*-ethyl-biguanide chloride $Cu(C_4H_{11}N_5)_2\ Cl_2.0.5H_2O$.		15.82	34.87	17.59	15.87	34.90	17.63
4.	Copper *bis*-phenyl-biguanide chloride $Cu(C_8H_{11}N_5)_2\ Cl_2.H_2O$.	Ray & Chakravarty, this *Journal*, 1941, **18**, 609.	12.54	27.64	14.05	12 53	27.65	14.03
5.	Copper *bis*-dimethyl-biguanide chloride		14.45	31.85	16.15	14.48	31.90	16.17
6.	Copper *bis*-diethyl-biguanide chloride $Cu(C_6H_{15}N_5)_2\ Cl_2.1.5H_2O$.	Ray & Ghosh, *ibid.*, 1949, **26**, 144.	13.35	29.44	14.95	13.55	29.50	15.05
7.	Copper ethylene-dibiguanide chloride $Cu(C_6H_{16}N_{10})\ Cl_2.1.5H_2O$.	Ray & Ghosh, *ibid.*, 1943, **20**, 291.	16.43	...	18.30	16.45	...	18.32
8	Copper *m*-phenylene-dibiguanide chloride $Cu(C_{10}H_{16}N_{10})Cl_2\ 1\ 5H_2O$.	Ray & Siddhanta, *ibid.*, 1943, **20**, 200.	14.52	32.00	16.23	14.55	32 02	16 22
9.	Nickel *bis*-biguanide chloride $Ni(C_2H_7N_5)_2\ Cl_2.2H_2O$.	Ray & Purkayastha, *ibid.*, 1941, **18**, 217.	15.37	38.03	19 40	16.01	38.00	19.46
10.	Nickel *bis*-methyl-biguanide chloride $Ni(C_3H_9N_5)_2\ Cl_2.4.5H_2O$.		13.31	31.98	16 10	13.35	32.01	16.14
11.	Nickel *bis*-ethyl-biguanide chloride $Ni(C_4N_5H_{11})_2\ Cl_2.0\ 5\ H_2O$.		14.79	35.29	17 89	14 82	35.32	17.89
12.	Nickel *bis*-phenyl-biguanide chloride $Ni(C_8H_{11}N_5)_2\ Cl_2\ 2.5H_2O$.	Ray & Chakravarty, *loc. cit.*	11.10	26.48	13 43	11.14	26.50	13.41
13.	Nickel *bis*-dimethyl-biguanide chloride $Ni(C_4H_{11}N_5)_2\ Cl_2.0\ 5H_2O$.		14.09	33.59	17.04	14.08	33.60	17.09
14.	Nickel *bis*-diethyl-biguanide chloride $Ni(C_6H_{11}N_5)_2\ Cl_2.0.5H_2O$.		12.96	30.92	15.66	12.99	30.98	15.67
15.	Nickel ethylene-dibiguanide chloride	Ray & Ghosh, *loc. cit.*, 1943,	15.31	...	18.50	15.30	...	18.48

TABLE II

Decomposition of copper bis-*phenylbiguanide chloride.*

$C = 0.01M.$ Temp. = 32°.

C_E.	p_H.	$BigH_2^+ \times 10$.	$X.10^3$.	$\bar{n}$.	$\log(BigH_2^+/H^+)$.	$k_1 \times 10^{-1}$.	$k_2 \times 10^{-3}$.
0.0025	5.09	2.499	2.500	1.750	3.488		1.024
0.0040	5.64	3.995	3.997	1.600	3.242	...	1.160
0.0050	5.38	4.994	4.996	1.500	3.078	...	1.196
0.0060	5.15	5.982	5.987	1.401	2.957	...	1.351
0.0075	4.87	7.457	7.471	1.253	2.743	...	1.637
0.0100	4.38	9.837	9.897	1.010	2.373	...	2.268
0.0125	3.97	12.010	12.200	0.780	2.050	3.162	
0.0150	3.60	13.730	14.220	0.578	1.738	3.989	
0.0175	3.27	14.730	15.820	0.418	1.458	3.989	
0.0200	3.05	15.090	17.030	0.297	1.229	4.007	

$k'_1 = 4.524 \times 10^1$: $k'_2 = 1.076 \times 10^3$ from Fig. 1 (after correction)

Expt. mean of $k'_1 = 3.5189 \times 10^1$.

$k'_2 = 1.436 \times 10^3$.

$K = k_1.k_2 = k'_1.k_1^*.k'_2k_1^* = 1.77 \times 10^{-17}$.

FIG. 1

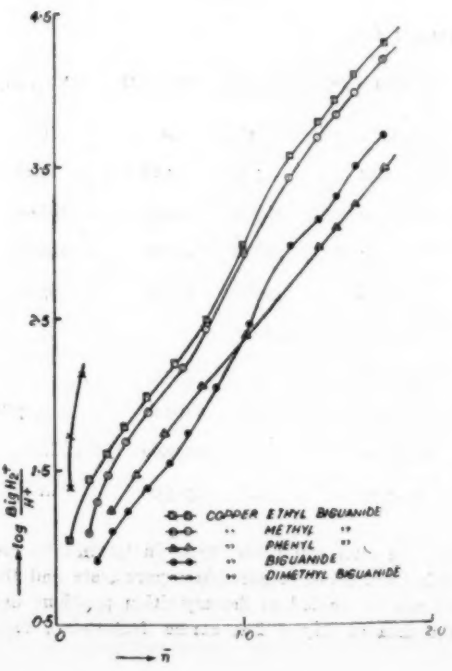


FIG. 2

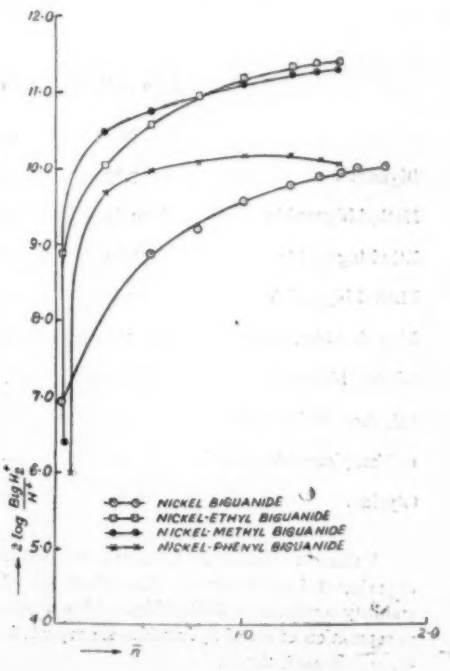


TABLE III

Formation of copper phenylbiguanide.

Cu^{2+} = 0.01*M*. p_H of 0.01*M*-phenylbiguanide chloride solution = 5.70.

Temp. = 32°. p_H of 0.01*M* copper chloride solution = 4.71.

$BigH_2^+$ added.	KOH added.	p_H.	$BigH_2^+ \times 10^2$	BigH-in complex $\times 10^3$.	$k't_1 \times 10^2$.	$kt_2 \times 1$
0.0050		3.15	0.366	1.080	2.043	
0.0100	...	3.14	0.760	1.606	1.742	
0.0150	...	3.12	1.082	2.119	1.884	
0.0200	...	3.11	1.562	2.620	1.765	
0.0250	...	3.11	1.971	3.063	1.740	
0.0175	0.0150	5.83	0.227	14.970	—	6.442
0.0200	0.0150	5.47	0.502	14.970	—	6.679
0.0225	0.0150	5.29	0.736	14.980	—	6.917
0.0250	0.0150	5.02	0.999	14.980	—	9.143

Mean of $k't_1$ = 0.01835 ; $k't_2$ = 0.00073.

giving for $K = 2.58 \times 10^{-17}$.

TABLE IV

	$k_1^{Cu} .10^{11}$.	$k_2^{Cu} .10^9$.	$K^{Cu} .10^{19}$.	$K^{Ni} .10^{14}$.	$K^{Cu} .10^{19}$.	$K^{Ni} .10^{14}$.
	(1)	(2)	(3)	(4)	(5)	(6)
Biguanide	7.87	5.76	4.54	3.31	4.68	2.86
Methyl biguanide	29 85	23.62	70 52	166 00	69.20	168.00
Ethyl biguanide	36.84	27.65	101.90	166.30	105.80	149.20
Phenyl biguanide	85.21	20.50	177.00	524.80	177.30	563.20
Dimethyl biguanide	241.50(319.90)	(85.00)	(2722 00)	(4266.00)	—	...
Diethyl biguanide	(1045.00)	1467.70)	(489700.00)	...	—	...
Ethylene dibiguanide	...	...	0.0022	0.0708	0.0021	0.0786
***m*-Phenylene dibiguanide**	...	...	36310.00	...	31452.00	...
Glycine	660.60	141.30	9333.00	...	9323.00	...

Values in columns (1) to (4) are obtained from Figs. 1-4 after correction; those in (5) and (6) are experimental mean values. Ni-*m*-phenylene dibiguanide could not be prepared in a pure state and the stability constants of dialkyl biguanide complexes could not be studied as decomposition reactions due to separation of metal hydroxides are reported from the data of Ray & Das Sarma (*Naturwiss.*, 1955, **42**, 415) in parenthesis.

FIG. 3

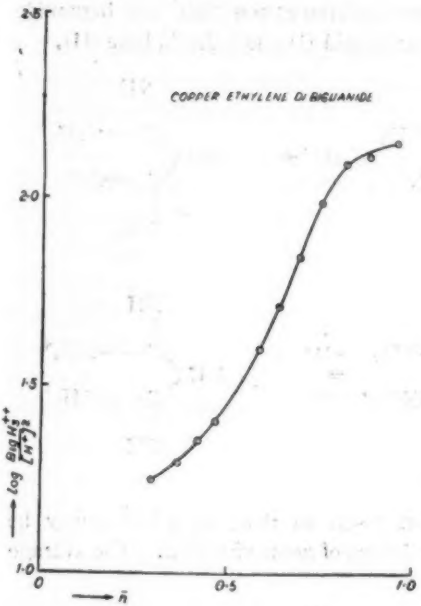


FIG. 4

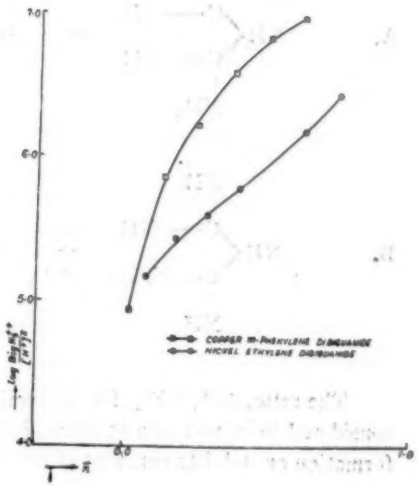


TABLE V

	pk_1^*.	pk^*_{av}.	pk_1^{cu}.	pk_2^{cu}.	$\frac{pk_1^{cu}}{pk_2^{cu}}$.	pk_{av}^{cu}.	pk_{av}^{xi}.	$\frac{pk_{av}^{cu}}{pk_1^*}$.	$\frac{pk_{av}^{Ni}}{pk_1^*}$.
Big[a]	11.52	7.23	10.10	8.24	1.23	8.17	6.74	0.80	0.58
MeBig[a]	11.44	7.22	9.53	7.63	1.25	8.58	5.89	0.75	0.51
Et Big[a]	11.47	6.78	9.43	7.56	1.25	8.50	5.89	0.74	0.51
PhBig[a]	10.72	6.44	9.07	7.69	1.18	8.38	5.64	0.78	0.53
DiMe Big[a]	11.52	7.15	8.50	7.07	1.20	7.79	5.28	0.68	0.46
DiEt Big[a]	11.68	7.11	7.98	6.33	1.26	7.15	...	0.61	...
Ethylene diBig[a]	11.55	6.87[d]	...	...	...	10.83	7.58	0.94	0.66
m-Phenylene diBig[a]	10.63	6.20[d]	...	...	...	7.22	...	0.68	...
Glycine[a]	9.55	5.90	8.13	6.85	1.19	7.54	...	0.79	...
Ethylenediamine[b]	9.92	8.60	10.55	9.05	1.06	9.80	6.90	0.99	0.70
Salicylaldehyde[c]	9.50	8.45	7.50	5.80	1.29	6.65	4.56	0.70	0.48

a—present investigation ; b-Carlson, McReynolds & Verhock, *J. Amer. Chem. Soc.*, 1945, **67**, 1334.

c—Calvin & Wilson, *ibid.*, 1945, **67**, 2003.

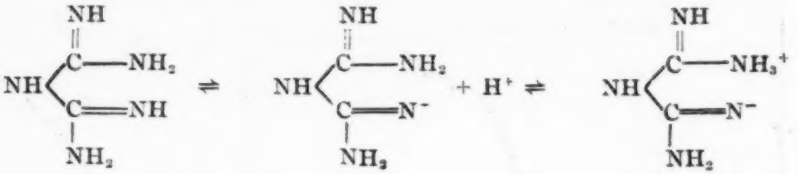
d—$1/2\ (pk_1^* + pk_2^*)$ values.

e—Ray & Das Sarma, *Naturwiss.*, 1955, **42**, 415. $pk_{av} = 1/n\ (pk_1 + pk_2 + \ldots\ \ldots + pk_n)$.

DISCUSSION

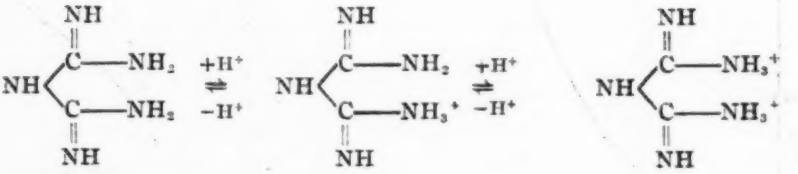
It has already been pointed out in an earlier communication that the biguanide molecule behaves as an ampholyte acting as a potential acid (I) and a diacid base (II).

A.



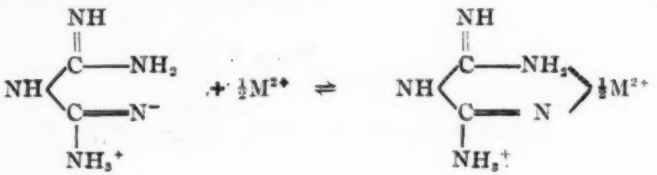
(I)

B.

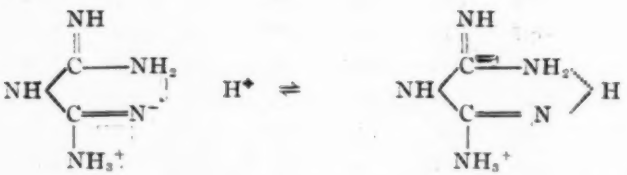


(II)

The ratio, pk^*_1/pk^*_2, for biguanides is about $4 \sim 5$, so that, as a base it may be considered to behave as a mono-acid one, to a fair degree of approximation. The average formation or stability constant of the system,



may be compared with



so that, we may expect a rough proportionality between the first acid-dissociation constant and the average stability of the complex formed with the base, arguing after Calvin and co-workers (*loc. cit.*).

This point has been elucidated by Bjerrum (*Chem. Rev.*, 1950, **46**, 386) showing that the ratio log k_M/log k_H (where k_M = AH/A.H and k_M = the mean complexity constant of the metal) is 0.35 – 0.40 for Ag, 0.78 – 0.87 for Hg for ligands with one point of attachment, though values 0 22 for the first and 0.96 have also been recorded for the two groups of systems respectively. Calvin and Wilson (*loc. cit.*) have similarly given a ratio of 0.9 for β-diketones and 0.6 – 0.7 for salicylaldehyde complexes of copper.

In the present case, more or less concordant values of the ratio log k_M/log k_B has been obtained with X_B as the first acid-dissociation constant.

But it can be examined further purely from the point of view of energetics. Hydrogen, as is well known, is incapable of forming two stable covalent bonds, as it can have only one stable orbital. The two cases are therefore not exactly parallel.

It is obvious that there is some optimum basic strengths for ligands. Too strong an acid or two strong a base will tend to form ionic bonds, and hence, will not be suitable for the formation of covalent complexes.

A comparison of the data in Table V at once reveals some interesting points, *i.e.*, the abnormally high values (0.94 – 0.99 and 0.66 – 0.7) of log k_M/log k_B ratio for ethylene dibiguanide and ethylenediamine as ligands. This deviation from the normal value (0.7-0.8 and 0.51-0.58) may be somehow connected with the occurrence of five-membered rings in the complexes formed. The lower value with *m*-phenylenedibiguanide-Cu system might be attributed to steric factors.

The values for the stability of the copper biguanide complexes lie at about 10^4 to 10^6 times greater than those for the corresponding nickel compounds. It has further been found that while copper complexes suffer stepwise decomposition, affording well defined instability constants k_1^{Cu} and k_2^{Cu} for the mono- and *bis*-biguanide complexes respectively, the corresponding nickel complexes show more or less a single-step decomposition. Moreover, no colour changes have been observed in the case with those of copper (Das Sarma and Rây, this *Journal*, 1951, **28**, 347). The decomposition of dibiguanide complexes of both copper and nickel, however, are quite satisfactorily respresented in the form of a single-stage process:

$$MA^{2+} + 2H^{+} \rightleftharpoons M^{2+} + AH_2^{2+}$$

where A represents a quadridentate dibiguanide molecule. Further discussion on these apparent one-step formation and dissociation of nickel *bis*-biguanide, copper dibiguanide and nickel dibiguanide complexes will follow in a subsequent communication.

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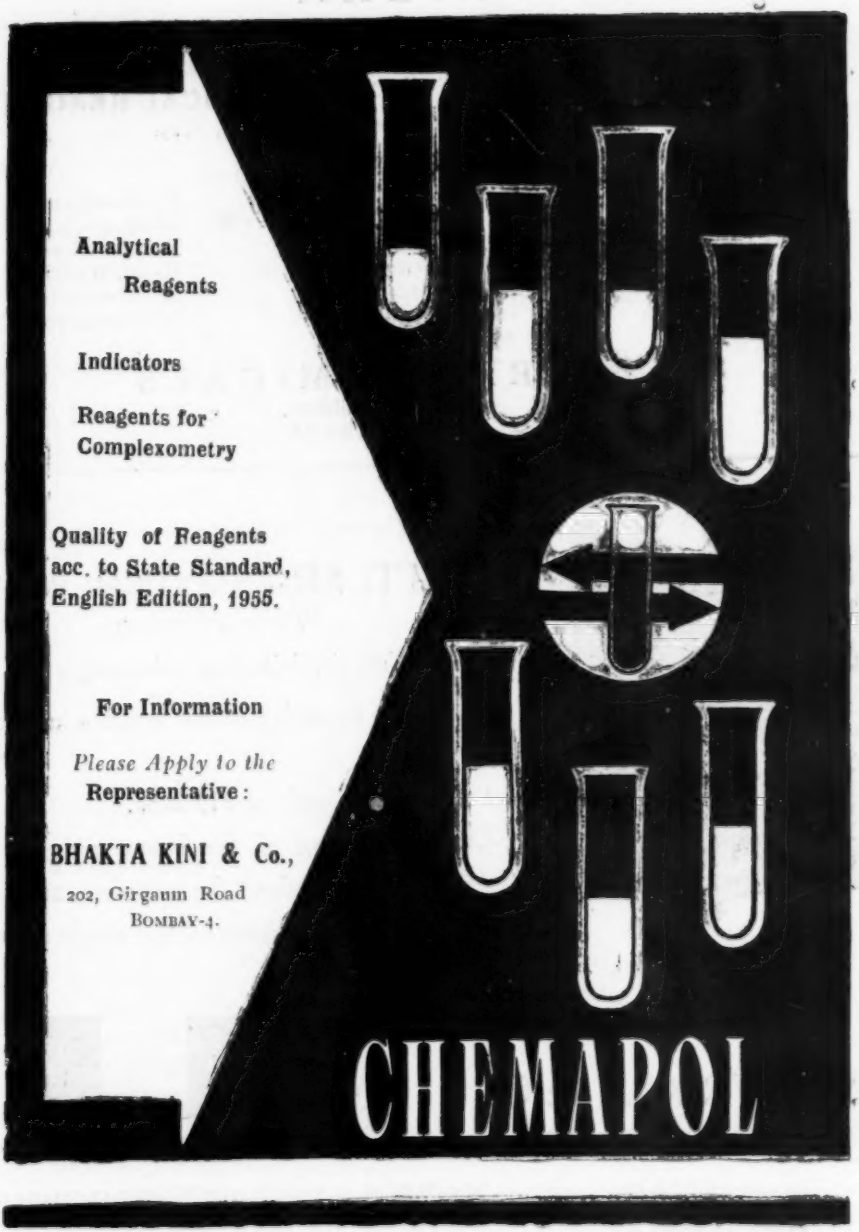

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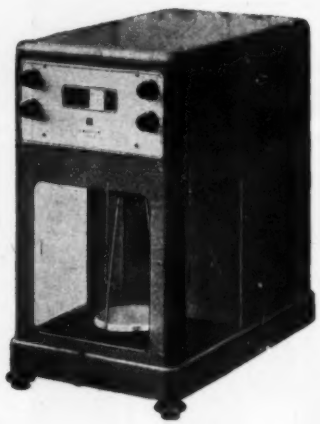

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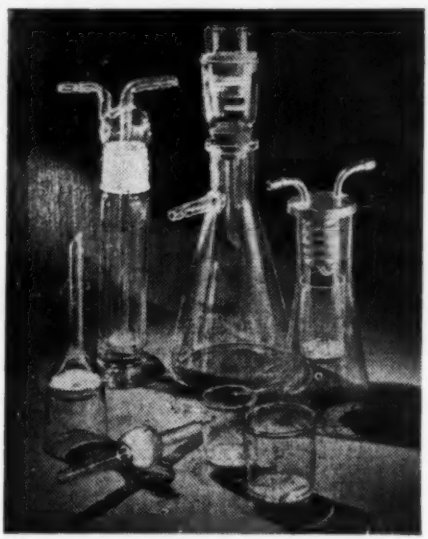

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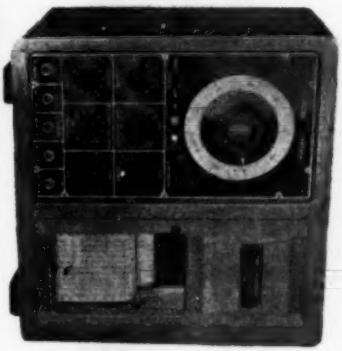

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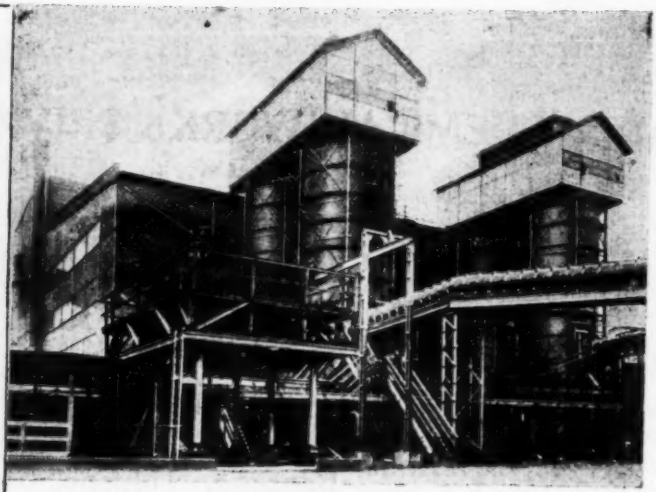

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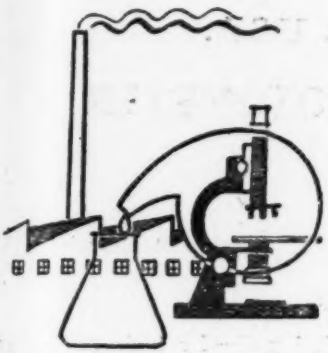

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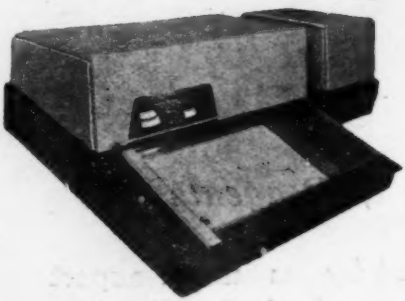

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